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## Reductive Depolymerization of Kraft Lignin for Chemicals and Fuels Using Formic Acid as a In-Situ Hydrogen Source

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Graduate Program in Chemical and Biochemical Engineering  
A thesis submitted in partial fulfillment of the requirements for the degree in Master of Engineering Science  
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**REDUCTIVE DEPOLYMERIZATION OF KRAFT LIGNIN FOR  
CHEMICALS AND FUELS USING FORMIC ACID AS AN *IN-SITU*  
HYDROGEN SOURCE**

(Thesis format: Integrated Article)

by

Shanhua Huang

Graduate Program in Chemical and Biochemical Engineering

A thesis submitted in partial fulfillment  
of the requirements for the degree of  
Mater of Engineering Science

The School of Graduate and Postdoctoral Studies  
The University of Western Ontario  
London, Ontario, Canada

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## Abstract

In this thesis work, formic acid (FA) proved to be an effective *in-situ* hydrogen donor for the reductive depolymerization of kraft lignin (KL). At the optimum conditions without catalysts, i.e., 300 °C, 1 h, 18.6 wt.% substrate concentration, 50/50 (v/v) water-ethanol medium at a FA-to-lignin mass ratio of 0.7, KL ( $M_w \sim 10,000$  g/mol) was effectively depolymerized, producing depolymerized lignin (DL,  $M_w$  1, 270 g/mol) at a yield of ~90 wt.% and <1 wt.% yield of solid residue (SR). The effects of heterogeneous catalysts on KL reductive depolymerization in 50/50 (v/v) water-ethanol medium were also investigated. At all conditions, FHUDES-2 (W-Mo-Ni) catalyst showed very high efficiency in sulfur-removal, and Ru<sub>10%</sub>/C exhibited excellent activity for depolymerization and hydrogenation of the depolymerized lignin products. However at a lower temperature (200 °C), Ni<sub>10%</sub>/Zeolite catalyst demonstrated superb catalytic activity for reductive depolymerization of KL, producing 93.5(±4.1) wt.% yield of DL of  $M_w = 3150$  g/mol.

## Keywords

Depolymerization, formic acid, kraft lignin, depolymerized lignin, hydrogen, catalyst

## Co-Authorship Statement

Chapters 3 and 4 are manuscripts submitted to peer-reviewed journals for consideration of publication. The contribution of each author is stated below.

### **Chapter 3:**

#### **Reductive Depolymerization of Kraft Lignin for Chemicals and Fuels using Formic Acid as an *In-situ* Hydrogen Source**

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Status: Accepted by *Bioresource Technology* in August 2014, currently the paper is in press.

Experimental work and data analysis were performed by Shanhua Huang under the supervision of Dr. Chunbao (Charles) Xu and Dr. Zhongshun Yuan. Matthew Tymchyshyn and Nubla Mahmood provided consultation regarding experimental work and interpretation of results. The manuscript was drafted by Shanhua Huang, and reviewed and revised by all co-authors.

### **Chapter 4:**

#### **Reductive Depolymerization of Kraft Lignin for Bio-chemicals or Fuels in Formic Acid with Supported Metal Catalysts**

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Status: Submitted to *Applied Catalysis B: Environmental*

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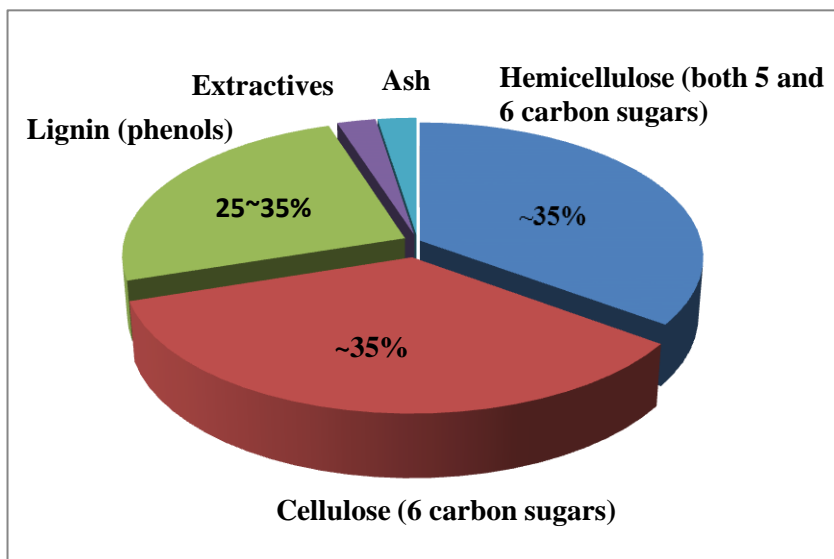
## Preface

*“If we knew what we were doing it wouldn’t be research” - Albert Einstein*

## Chapter 1 Introduction

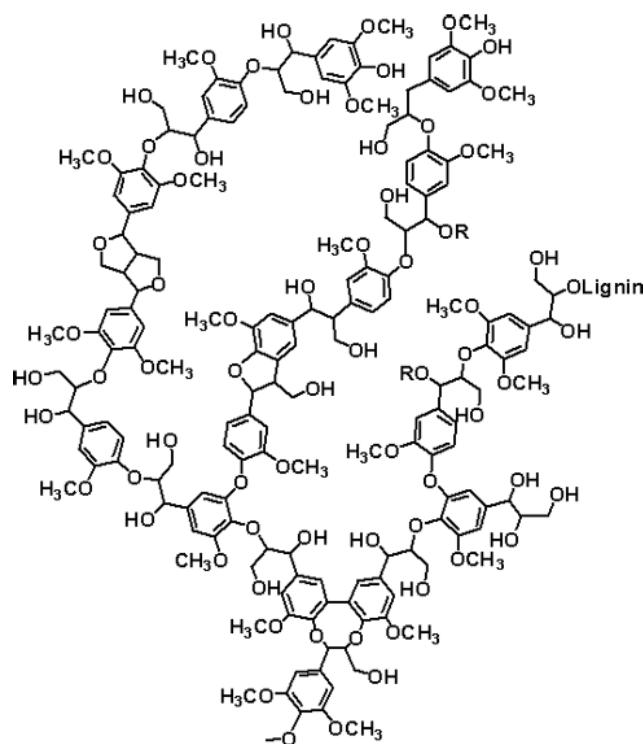
### 1.1 Lignin and its utilizations

Lignocellulosic biomass such as wood and crop residues consists of three main components (lignin, cellulose and hemicellulose), and a small amount of other components (ash and extractives). Typical composition of a woody biomass is shown in Figure 1-1, from which it can be seen that a wood biomass is comprised of 25-30 wt% lignin, ~35 wt% cellulose, ~35 wt% hemicellulose and 0-5wt% (extractives + ash).



**Figure 1- 1** Typical composition of a woody biomass

Lignin provides support and rigidity to the cell walls and is more resistant to most forms of biological attack in comparison with cellulose and other polysaccharides ([Akin and Benner, 1988](#); [Baurhoo et al, 2008](#); [Kirk, 1971](#)). It constitutes 15-30 wt% of the lignocellulosic biomass (wood or crop residues) and is a natural polymer made up mainly by three basic phenylpropane units (monomer), namely guaiacyl alcohol (G), syringyl alcohol (S), p-coumaryl alcohol (H) ([Mohan et al., 2006](#)). A model structure of lignin can be illustrated in Figure 1-2.



**Figure 1- 2** Model structure of lignin (Lignoworks,

<http://www.lignoworks.ca/content/what-lignin>. No copyright permission is needed)

To date, enzymatic hydrolysis of lignocellulosic biomass in the ethanol plants has made it possible to separate celluloses and hemicelluloses from the whole biomass, leaving lignin (may be called hydrolysis lignin, or HL in short) (in average 15-30 % by weight, 40 % by energy) as by-products (Perlack et al., 2005). Kraft lignin (KL) – another type of lignin is produced in large amount in the form of “black liquor” in the kraft pulping industry, mainly utilized in recovery boilers for heat and power generation in pulp/paper mills. According to the International Lignin Institute, worldwide about 40-50 million tons of kraft lignin is generated each year, and the production of the “black liquor” exceeds the demands for generating energy to fulfill the operation of paper mills. This has become a bottleneck for the kraft pulping industry (accounting for 60-70% of North American kraft mills) due to the surplus of lignin generation and limited recovery boilers’ capacity.

Currently, only lignosulfonates are used to produce a variety of value-added products for specialty products such as concrete additives, and dispersants in oil well drilling fluids. (Mark, 1938; Kelly, 1983). Lignins produced from kraft process or soda process are

mainly burned as low value fuel for energy generation, while kraft pulping process is the predominating process in pulp and paper industry. Thus, intensive research has been being carried out to investigate valorization of kraft lignin for various high-value chemicals such as antioxidants, antimicrobial, antifungal agents (Cruz et al., 2001), flame-retardants (Reti et al., 2008), or anti-sunlight/frost coating (Miidla, 1980) and UV-absorbent films (Liu et al., 2014).

However, the lower reactivity and high steric hindrance effects, caused by its branched structure, limits the direct use of lignin for the replacement of petroleum-based materials. New methods are developing to increase the value of lignin-based products. One of the most effective approaches to increase lignin's chemical reactivity and decrease its steric hindrance effects is to de-polymerize lignin into oligomers and aromatic chemicals, for the production of bio-based phenolic adhesives, polyurethane foams, flocculants and epoxy coating and their properties were found to be similar or perform even better than the petroleum-based products (Khitrin et al., 2012; Cheng et al., 2013).

Various lignin depolymerization processes have been reported in the literature. Lignin depolymerization methods mainly include biological method using enzyme and thermal method using heat (such as pyrolysis) and thermochemical methods using heat and chemicals, such as hydrolytic depolymerization using water and alkaline catalyst and reductive depolymerization using hydrogen. Among those methods, biological process is a very slow process, while pyrolysis operated at 400-800°C is fast, but lignin pyrolysis resulted in a low oil product yield (20-40 wt.%) with high energy consumption in particular for wet feedstocks (Pandey et al., 2008). In contrast, hydrolytic depolymerization of lignin operates under milder conditions requiring moderate temperatures (200-300°C) but higher pressures (50-150 bar). Hydrolytic depolymerization of lignin can be realized through the hydrolytically cleavage of ether bonds in lignin catalyzed by an acid or base catalyst (Yuan et al., 2010).

Reductive depolymerization of lignin is achieved by cleaving the ether bonds present in the lignin molecules with hydrogen molecules or atoms. In this process, an organic solvent and a supported catalyst (such as expensive carbon-supported Pt or Ru catalysts)



is needed (Yan et al., 2008). In a recent thesis work by Cheng from our group (Cheng, 2011), formic acid was employed in the depolymerization of alkali lignin (AL) and organosolv lignin (OL) in a water-ethanol (50/50, v/v) medium at 300-350 °C, obtaining 70-80% DL yields.

## 1.2 Thesis objectives

The overall objective of the research conducted for this thesis was to investigate the effect of formic acid addition and catalyst on lignin depolymerization in water/ethanol co-solvent at moderate temperature (200-350 °C). Continuing the work of Cheng (2011), this thesis work aimed to perform a systematic study on the reductive depolymerization of kraft lignin in ethanol-water and as co-solvent with formic acid under various conditions (temperature, pressure, reaction time, and ethanol concentration in the ethanol-water reaction media, and types of heterogeneous catalysts).

## 1.3 Thesis overview

Chapter 1 provides a short discussion about the importance of utilization of lignin for value-added bioproducts (bio-fuels, bio-chemicals and biomaterials), and presents an overview of the sources, industrial production and current utilizations of lignin and various depolymerization processes to increase lignin's chemical reactivity and decrease its steric hindrance effects.

Chapter 2 presents a comprehensive review of literature on valorization of lignin for energy, fuels and chemicals..

Chapter 3 and 4 presents results from experimental work from reductive depolymerization of kraft lignin in ethanol-water and as co-solvent with formic acid under various conditions (temperature, pressure, reaction time, and ethanol concentration in the ethanol-water reaction media, and types of heterogeneous catalysts). Chapter 3

focuses on the optimization of reaction parameter (e.g., reaction, temperature, time, solvent composition, and substrate concentration, as well as the amount of formic acid). Chapter 4 aimed at lowering the reaction temperature and pressure by using heterogeneous catalysts.

Chapter 5 provides overall conclusions from this thesis research.

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## Chapter 2 Valorization of Lignin for Chemicals and Materials - Literature Review

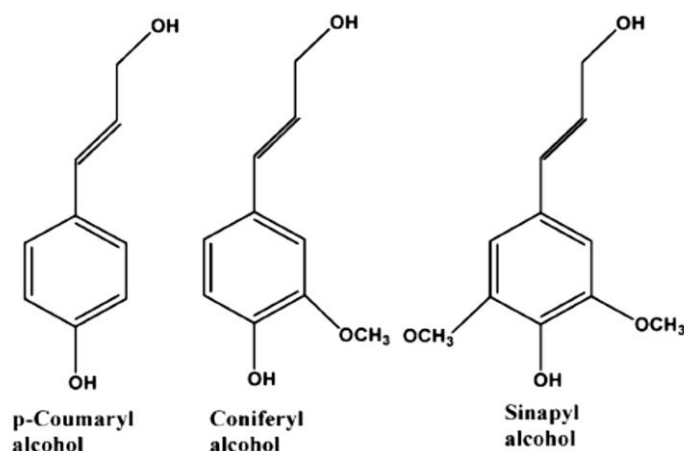
### 2.1 Lignin – A Potential Source for Chemicals and Materials

There are increasing concerns worldwide over declining non-renewable fossil resources, energy security, climate change and sustainability. It is thus of strategic significance to explore alternatives to fossil resources for energy, but particularly for chemicals production. Among all the potential alternatives to fossil resources, lignocellulosic biomass such as wood and wood waste, forestry residues (limbs, bark, sawdust, etc.) are promising because they are on non-food basis, immense, renewable, and hence sustainable sources for both energy and chemical production.

Chemicals and materials much more valuable than energy and fuels according to a lesson learnt from petroleum industry, where 70% of crude oil is used for transportation fuels and only 4% for chemicals, plastics and rubbers. However, almost equal amounts of revenues (~\$380 billion, respectively) are generated from the sector of transportation fuels and that of the chemicals/plastics/rubber. As reported by [Bhima \(2011\)](#), the three trillion dollars global chemical market will be occupied by bio-derived chemicals up to 15% in 2025. As such, exploring technologies to produce bio-chemicals and biomaterials from lignocellulosic biomass will yield both environmental and economic benefits.

As briefly described in Chapter 1, typically a woody biomass is comprised of 25-30 wt% lignin, ~35 wt% cellulose, ~35 wt% hemicellulose and 0-5wt% (extractives + ash) as shown in the previous Figure 1-1. Lignin provides support and rigidity to the cell walls and is more resistant to most forms of biological attack in comparison with cellulose and other polysaccharides ([Akin and Benner, 1988](#); [Baurhoo et al, 2008](#); [Kirk, 1971](#)). It constitutes 20-30 wt% of the lignocellulosic biomass and is made up mainly by three basic phenylpropanol units (monomer), namely guaiacyl alcohol (G), syringyl alcohol

(S), p-coumaryl alcohol (H) (Mohan et al., 2006), whose structure is presented in Figure 1-1.



**Figure 2- 1** Structure of p-coumaryl, coniferyl, and sinapyl alcohols , reprinted (adapted) with permission from (Mohan et al., 2006). Copyright © 2006, American Chemical Society.

The actual structure of lignin also depends on the plant origin. For example, softwood lignins are made up of mainly guaiacyl units (coming from coniferyl alcohol) while hardwood lignins contain various ratios of guaiacyl and syringyl units (Rohella et al., 1997). However, grass lignin is comprised of all types of monomers, i.e., all guaiacyl, syringyl and p-hydroxyphenyl units.

As also presented in the model structure of lignin (Figure 2–1), lignin contains mainly  $\beta$ -O-4 aryl ether,  $\alpha$ -O-4 aryl ether, 4-O-5 diaryl ether,  $\beta$ -5 phenylcoumaran, 5-5 biphenyl,  $\beta$ -1-(1,2-Diarylpropane) and  $\beta$ - $\beta$ -(Resinol) linkages, depending on the source of lignin such as softwood and hard wood, as shown in Table 2-1 (Pandey and Kim, 2011). Compared with hardwood lignin, softwood lignin contains less  $\beta$ -O-4 aryl ether (a relatively weak linkage) and more 5-5 biphenyl linkage (a strong C-C linkage), thus it is more difficult to decompose or de-polymerize.

**Table 2- 1** Proportion of major linkages in lignin, reprinted (adapted) with permission from (Pandey and Kim, 2011). Copyright © 2011 Wiley.

Linkage type	Softwood (spruce) [%]	Hardwood (birch) [%]
$\beta$ -O-4-Aryl ether	46	60
$\alpha$ -O-4-Aryl ether	6–8	6–8
4-O-5-Diaryl ether	3.5–4	6.5
$\beta$ -5-Phenylcoumaran	9–12	6
5-5-Biphenyl	9.5–11	4.5
$\beta$ -1-(1,2-Diarylpropane)	7	7
$\beta$ - $\beta$ -(Resinol)	2	3
Others	13	5

## 2.2 Industrial Production of Lignin

In the ethanol plants, lignin is separated from lignocellulosic biomass through enzymatic hydrolysis where celluloses and hemicelluloses are separated from the whole biomass, leaving lignin (hydrolysis lignin, HL) as by-products (Perlack et al., 2005). In the kraft pulping industry, kraft lignin (KL) as another type of lignin is produced in large amount in the form of “black liquor”. According to the International Lignin Institute, about 40-50 million tons of kraft lignin is generated worldwide each year. KL-containing “black liquor” is mainly utilized in recovery boilers for heat and power generation. However, the production of the “black liquor” exceeds the demands for generating energy to fulfill the operation of paper mills, and 60-70 % of North American kraft mills have a bottleneck in recovery boilers capacity due to the surplus of lignin generation and limited recovery boilers’ capacity.

A moderate-capital solution to the above problem is to precipitate some portion of kraft lignin from the black liquor, which would increase incremental pulp production and provide an additional revenue stream from the sale of the isolated kraft lignin. While

currently worldwide 1-1.5 million tonnes/year of lignin is employed for a wide range of applications ([Lora and Glasser, 2012](#)), almost all of this is lignosulfonates from sulfite pulping. Lignosulfonates are water-soluble, and highly sulfonated substances, quite different from kraft lignin. Until recently, the only commercial source of kraft lignin has been from Mead-Westvaco, which produces approximately 20,000 metric tons/year of kraft lignin under the trade name Indulin from a plant in South Carolina. However, in the first half of 2013, Domtar has begun operation of a 75 tonnes/day kraft lignin plant at its mill in Plymouth, North Carolina. In addition, FPIInnovations has successfully developed a proprietary lignin extraction process – LignoForce™ systems, and a lignin pilot plant (in a capacity of 100 kg/day) in Thunder Bay, ON has been running for more than two years. This provides tremendous opportunities for the utilization of kraft lignin for value-added applications such as biofuels, bio-chemicals and biomaterials, which would help to create additional revenue stream for the pulp and paper industry.

Not surprising, the type of the pulping processes affects the structure of lignin resulted from the pulping process, owing to different chemical transformation reactions involved during the pulping ([Doherty et al., 2011](#)). For instance, lignosulfonate is produced from sulfite process where wood chips undergo an acidic liquid containing sulfur dioxides at 140 and 160 °C for liberating lignin. The lignosulfonate is highly cross-linked and have two types of ionizing functional groups: sulfonate and phenolic hydroxyl group, due to the extended lignin chains formed in the process of the sulfite delignification ([Doherty et al., 2011](#)). Thus, the lignin produced from this process is water-soluble, making it good commercial dispersants. In kraft or soda pulping processes, however, wood chips are heated up to 150 and 170 °C in an alkaline liquid (so-called “white liquor”), where lignin is separated from cellulose and hemicelluloses. Then the white liquor (alkaline liquid) turns into “black liquor”, and is evaporated in multiple effect evaporators before it is burned in a recovery boiler for recovery of the inorganic chemicals and generation of heat and power.

Lignin in the black liquor can be separated by precipitation using a strong acid. Patented lignin precipitation processes (Lingoboost and Lignoforce processes) have been developed, replacing the strong acid by carbon dioxide in order to increase the



environmental positive gains. Lignins produced from kraft pulping process were found to contain more phenolic hydroxyl groups and had a weight-average molecular weight ( $M_w$ ) of  $\sim 10,000$  (Schorr et al., 2014). To the contrary, soda lignins contain a high carboxylic acid content, making it a good candidate for dispersants (Doherty et al., 2011). Other pulping processes, such as the Alcell process, employing organic solvents (e.g., ethanol and water) to remove lignin from cellulose, produces a low-sulfur and low molecular weight lignin, often called organosolv lignin.

Currently, only lignosulfonates are used to produce a variety of value-added products for specialty products such as concrete additives, and dispersants in oil well drilling fluids (Kelly, 1983). Lignins produced from kraft process or soda process are mainly burned as low value fuel for energy generation, while kraft pulping process is the predominating process in pulp and paper industry. Thus, intensive research has been carried out to investigate valorization of kraft lignin for various high-value chemicals such as antioxidants, antimicrobial, antifungal agents (Cruz et al., 2001), flame-retardants (Reti et al., 2008), or anti-sunlight/frost coating (Miidla, 1980) and UV-absorbent films (Liu et al., 2014).

However, the lower reactivity and high steric hindrance effects, caused by its branched structure, limits the direct use of lignin for the replacement of petroleum-based chemicals and materials. Chemical modifications or conversions of lignin are needed to enhance its reactivity and reduce the steric hindrance effects of lignin to facilitate the use of lignin for chemicals and materials. The following sections overview various lignin modification or conversion processes.

## 2.3 Gasification of Lignin into $H_2$ or Syngas

Gasification is a thermal transformation that converts carbonaceous materials in controlled atmosphere of oxygen and steam at high temperature ( $> 700\text{ }^\circ\text{C}$ ), into carbon monoxide, hydrogen and carbon dioxide. Though temperature over  $700\text{ }^\circ\text{C}$  is necessary for complete gasification of lignin in conventional air or steam gasification, low-temperature hydrothermal gasification was also investigated using sub-/supercritical

water as the reaction medium (Guo et al, 2007; Ji et al, 2007). For example, “black liquor” was gasified in supercritical water (SCW) (Naqvi et al, 2010). However, it was found that lignin cannot be completely gasified due to the existence of thermal stable phenolic units at low temperature (250-400 °C) (Osada et al, 2004). As a result, the gas yield of lignin is relatively low (~30 %). Although hydrothermal gasification of lignin is promising approach to produce syngas, this technology is still under investigation due to its technical immaturity.

The gas products from lignin gasification comprise mainly CO<sub>2</sub>, H<sub>2</sub>, CO, CH<sub>4</sub> with little amount of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. The gas products can be applicable in fuel cells, gas turbine and as syngas for chemical synthesis. Due to the existence of CO<sub>2</sub> and other impurities, separation/purification of the gas products is necessary for syngas application. Ji et al. (2006) reported that the use of 1-hexanol instead of water produced gas products of higher hydrogen purity. An effective approach for gas purification using iron oxide and calcium oxide packed beds were reported by Campen et al. (2007), where 99 wt.% hydrogen gas streams was obtained at 650 °C. The need of gas purification processes, the lower energy efficiencies plus the low gasification efficiencies at lower temperatures, make the lignin gasification processes expensive to build on an industrial scale (Calzavara et al., 2005).

## 2.4 Wet Oxidation

Wet oxidation is a thermal transformation where organic and inorganic chemicals are oxidized by oxidant in aqueous medium at elevated temperatures ranging from 100 to 400 °C and pressure from 0.5 - 20 MPa (Mishra, et al, 1995). The products of wet oxidation of lignin include aromatic aldehydes such as vanillin, syringaldehyde, and p-hydroxy-benzaldehyde.

It is important to separate useful chemicals from unreacted species in wet oxidation process. The common separation methods include liquid-liquid extraction (after acidification of the reaction medium to isolate the unconverted lignin and other lignin derived high molecular weight compounds), ultrafiltration membrane separation (an

effective way to isolate vanillin) and ion-exchange and crystallization ([Silva et al, 2009](#); [Zabkova et al, 2007](#)).

Vanillin is presently produced from lignin on an industrial scale in Norway by Borregaard company. However, this process might phase out due to its low vanillin yield (12-13 wt.%) and the challenges in waste treatment and other environmental issues. Moreover, the production cost of vanillin produced from lignin has been consistently at \$100-200 kg<sup>-1</sup>, which was much higher than the global market price of about \$15 kg<sup>-1</sup> ([Nair, 2005](#); [Triumph Venture Captical Ltd, 2004](#)), which makes the lignin-to-vanillin process not economically viable.

## 2.5 Pyrolysis of Lignin

Pyrolysis of lignin aims to obtain lower- molecular-weight liquid products (i.e., bio-oil or pyrolysis oil) and gas products (H<sub>2</sub>, CO, CO<sub>2</sub>, and CH<sub>4</sub>, etc.). In this process, lignin is heated up to high temperatures, usually around 550 °C in the absence of air for a short period of time. The bio-oil yield from lignin pyrolysis was around 30 wt.% it could replace 40 wt.% phenol in synthesis of phenol formaldehyde (PF) resins ([Roy et al, 2000](#)). The high yield of char (>50 wt.%) from lignin pyrolysis has intensified the research interest in finding applications of the lignin-derived chars to justify the economic feasibility of the process. Typical applications of the chars are as absorbents or catalyst support due to their porous nature ([Eddy et al., 2014](#)). Fluidized bed reactors are usually employed in the lignin pyrolysis process, which however requires pretreatments of lignin feedstock such as drying and pelletization, resulting in high capital investment. Another practical challenge of fluidized-bed pyrolysis of lignin is that feeding lignin into the reactor at elevated temperature could lead to clogging of the feeder due to melting of lignin ([Wiberink et al., 2011](#)). In the same study, it was demonstrated that blending lignin with clay could solve the clogging problems during feeding. In the author's Institute, the group of Drs. Franco Berruti and Cedric Briens have developed a novel pneumatically actuated pulse feeder that proves to be effective for feeding lignin into fluidized bed reactors without clogging.

## 2.6 Hydrothermal Liquefaction or Hydrolytic Depolymerization of Lignin

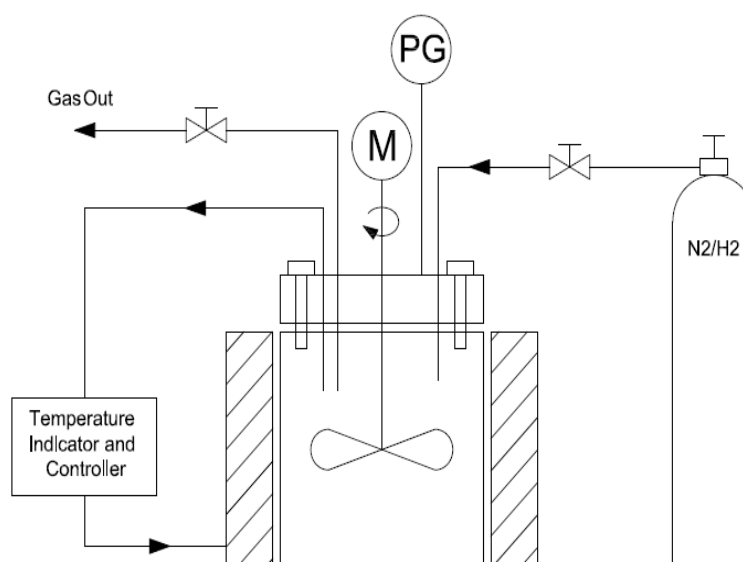
The concept of biomass hydrothermal liquefaction (HTL) process originated from coal liquefaction research in Germany more than a century ago. Lignin, a natural polymer containing aromatic/phenolic ring structures, is produced in a large amount as a byproduct from pulp and paper mills and ethanol plants. Many technologies, including the previously discussed pyrolysis and HTL or hydrolytic depolymerization discussed in this section, have been applied to liquefy (or de-polymerize) lignin into phenolic oils mainly as chemical feedstock for the production of bio-based phenolic resins, polyurethane and epoxy resins. As discussed previously, the oil yields are quite low in lignin pyrolysis processes, leaving a large amount of char. In contrast, HTL or hydrolytic depolymerization technology provides various benefits that are unparalleled in comparison with other technologies such as gasification, wet oxidation and pyrolysis. Hydrothermal liquefaction does not use severe reaction conditions as gasification and are flexible with moisture content, provided that drying of feedstock is always costly. Additionally, lower-oxygen oils (10% and 15%) can be produced from liquefaction as part of oxygen exists in organic compounds could be hydrolyzed into the aqueous phase (He et al, 2008).

The hydrolytic depolymerization mechanism involves cleaving of mainly the  $\beta$ -O-4 ether bond under base or water condition, accompanied with dealkylation of side chains and hydrolysis of methoxyl groups (Roberts et al., 2011; Cheng et al., 2012). Roberts et al. (2011) also reported that consecutive addition reactions such as aldol addition and condensation reactions of highly reactive phenolic and catecholic monomers would cause oligomerization of the depolymerized lignin (DL) products.

## 2.6.1 The Processes

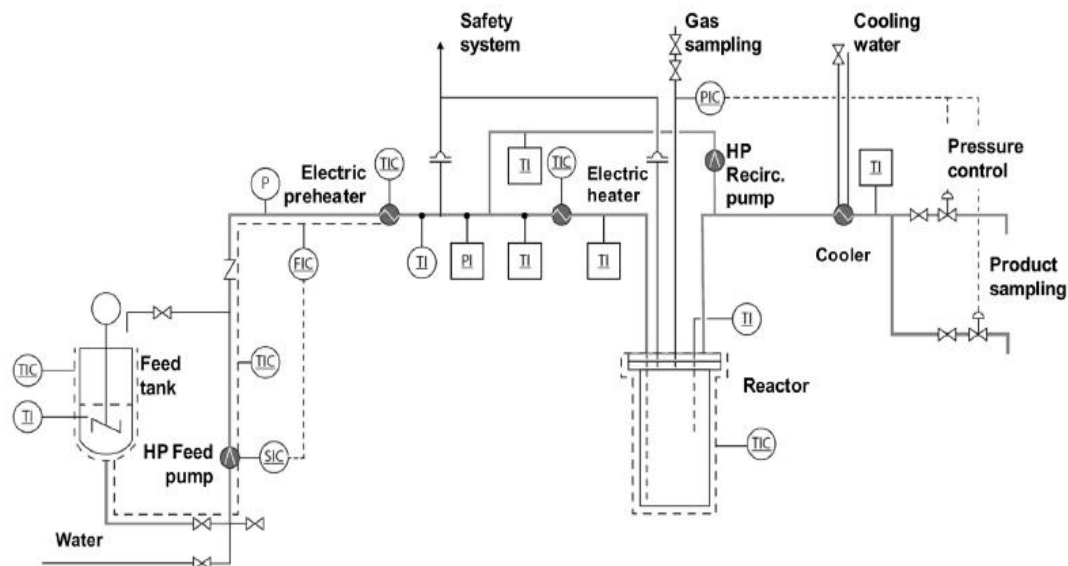
Lignin HTL or hydrolytic depolymerization process conditions such as substrate concentration, temperature, time, type of catalyst and solvent composition are reviewed by [Zakzeski et al. \(2010\)](#) and [Akhtar and Amin \(2011\)](#). The process is usually carried out in lab or pilot scale. Batch reactors and continuous flow reactors have been both used towards liquefaction/depolymerization of lignin into small molecules in literature ([Roberts et al., 2011](#); [Cheng et al., 2012](#); [Nguyen et al., 2014](#)).

Normally with a batch reactor, the desirable product yield is higher than that with other types of reactor. [Jin et al. \(2011\)](#) performed lignin depolymerization in a three-necked glass flask batch reactor, and the liquefaction efficiency reached 97 %. The obtained DL products have an OH number of 80-120 mg KOH/g, suitable to substitute polyols for the synthesis of polyurethane resins. [Cheng et al.\(2013\)](#) investigated the performance of three types of batch reactors, namely, stirred autoclave reactor, non-stirred reactor and shaken micro reactor for hydrothermal degradation of alkali lignin in sub/supercritical ethanol and water-ethanol co-solvent. It was demonstrated that solid residue (or char) formation could be prevented either by the stirring/shaking or by fast heating, although the molecular weight distribution of the DL products is not affected by the heating rate and stirring. A typical schematic diagram of a batch reactor system is showed below in Figure 2-1:



**Figure 2- 2** Sketch diagram of a batch reactor with a temperature PID controller and a stirrer

When it comes to continuous-flow reactor, the feeding of lignin is a challenge as it has to be crushed into smaller size for pumping and the concentration cannot be too high. [Nguyen et al. \(2014\)](#) depolymerized lignin in a continuous-flow reactor system using a low concentration, i.e., 5 wt.% lignin in water in pilot-scale continuous-flow reactor process, whose schematic diagram is presented below (Figure 2-2):



**Figure 2- 3** Schematic diagram of the continuous-flow process for lignin depolymerization, reprinted (adapted) with permission from (Nguyen et al., 2014).

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Compared with batch operation, continuous-flow reactor systems are more complex involving more reactor components/valves to avoid congestion of lignin and control the reactor pressure, as shown in above Figure 2-2. The products contained oil, aqueous phase and char. The oil yield in the process was as high as 70 wt.% with a char yield of 17-20 wt.% (Nguyen et al., 2014). In order to produce better quality of fragmented products and facilitate the continuous-flow operation, lignin was also first fragmented into small species in batch process before entering the fixed-bed reactor (Yoshikawa et al., 2013), where the yield of 1-ring aromatic compounds attained up to 27 wt.%. However, in Yoshikawa et al. (2013)'s work, the mass ratio of lignin to solvent was very low, as low as only 1:30, which is less economically attractive for operation in industrial scale.

In addition, base catalyzed depolymerization of lignin was carried out in a continuous flow reactor with lignin concentration of 5 wt.% by Roberts et al. (2011), obtaining a DL yield up to 52 wt.%. In another study by Beauchet et al.(2012), a higher yield of 72.1 wt.% oligomers with 10.8 wt.% monomers-rich fractions were produced with a continuous

flow reactor at 270 °C. Other types of reactors such as a semi-continuous tubular reactor (using crushed lignin particles and water solvent continuously fed in the reactor) were also investigated for lignin depolymerization ([Horacek et al., 2012](#)). The products yields at 380°C were found to be 20 wt.% solid residue, 30 wt.% in aqueous phase and 10 wt.% in oil phase (or DL).

In summary, batch reactors provide a simple and effective means for lignin HTL or hydrolytic depolymerization, but the batch processes are less efficient. The main challenge for a continuous-flow reactor is the clogging of the reactor system during the reaction due to char formation.

## 2.6.2 Composition and properties of depolymerized lignin

The hydrothermal liquefaction or hydrolytic depolymerization of lignin is still in lab scale, so the composition and properties of the DL products varied from one study to another. In general, the degraded products from lignin contain gaseous products, solid residue, some small aqueous products (such as organic acid compounds), oligomers-rich fraction and monomers-rich fraction. Separation of these fractions is time-consuming and labor-intensive, so in most studies, gas, aqueous phase and oil phase lumped products were separated. The aqueous phase usually comprises small organic acids and water-soluble monomers-rich fraction. The oil phase consists of mainly oligomers-rich fraction with a relatively higher molecular weight. The oligomers-rich phase makes up more than half of the DL products by weight. For example, [Beauchet et al.\(2012\)](#) reported that 72.1 wt.% oligomers-rich fraction and 10.8 wt.% monomers-rich fractions were produced using a continuous-flow reactor at 270 °C. The degraded lignin (DL) often refers to the oligomers-rich fraction with little amount of monomers-rich fraction.

Due to the wide distribution of fragmented products from lignin, molecular weight distribution can be a useful indicator for process optimization. Gel Permeation Chromatography (GPC) with a multi-angle laser light scattering (MALLS) detector or UV detector, Electrospray Ionisation Mass Spectrometry (ESI-MS) and Matrix-Assisted Laser Desorption/Ionization Time of Flight (MALDI-TOF) analysis are the most



common tools to measure the molecular weight distribution of the DL products. The weight-average molecular weight ( $M_w$ ) of DL products varies with different analytical methods. Those results from GPC-MALLS are believed to be more accurate than those from GPC-UV measurements based on polystyrene standard. Normally the DL products soluble in THF have a  $M_w$  of 10, 000-60, 000 g/mol (Cheng et al., 2013; Yuan et al., 2010), depending on the type of lignin on the reaction conditions. For example, Yuan et al. (2010) produced oligomers/polyols ( $M_w \approx 1000$  g/mol and  $M_n \approx 450$  g/mol) through hydrolytic depolymerization of alkaline lignin or kraft lignin ( $M_w \approx 60,000$  g/mol and  $M_n \approx 10,000$  g/mol) using NaOH in a water-ethanol mixture and phenol as a capping agent (lignin to phenol ratio = 1:1 (w/w)). With ESI-MS, the molecular weight of DL products was detected by in the range of 200-400 g/mol, which was similar to the structure of diesel fuel (Kleinert et al., 2009). However, this method fails to ionize many non-polar components such as alkanes and aromatics hydrocarbons. Song et al. (2013b) analyzed the DL products using MALDI-TOF. The research discovered that the lignin was first decomposed into smaller lignin species with molecular weight  $m/z$  ca. 1100 to ca. 1600 via alcoholysis before they were further depolymerized into monomeric phenols over Ni/C catalyst.

Gas Chromatography-Mass Spectrometry (GC-MS) is a useful tool to analyze the chemical compositions of the DL products. However, in most case, the DL products are composed of hundreds of chemicals with different structure and it is very difficult to determine compositions of all compounds using GC-MS. Moreover, the GC-MS has its own limitation in providing real composition of the DL products, as the degraded lignin contains significant amounts of high boiling-point oligomers, which cannot be detected by GC-MS due to their low volatility. For instance, the GC-MS spectra for DL products obtained with and without catalysts at 300 °C, particular in the 50/50 (v/v) water-ethanol co-solvent, had very few compounds detectable (Cheng et al., 2012). This implies that the depolymerized product at a relatively lower temperature was composed mostly of large oligomers molecules with a high boiling-point.

Also from the work of Cheng et al. (2012), the results of GC-MS analysis for two typical DL products obtained at 400 °C for 2 hr in pure ethanol and 50/50 (v/v) water-ethanol are

given in Table 2-2. As shown in the Table 2-2, only monomers and a few dimers were detectable in both DLs, while oligomeric products were not detectable due to their low-volatility. The compositions of the DLs are significantly different: The DL from the treatment with pure ethanol is rich in esters (total relative area percentage of ~44 %), phenolic derivatives (total relative area percentage of ~19 %), and alcohols (total relative area percentage of ~10 %). The esters might be generated by esterification between ethanol and some lignin-derived intermediates, as similarly observed by [Tang et al. \(2010\)](#) in catalytic hydrocracking of pyrolytic lignin to liquid fuel in supercritical ethanol. The subsequent major groups were monomeric phenolic compounds and derivatives, ascribed to the cleavage of  $C_\alpha/C_\beta$ , or  $C_\beta/C_\gamma$ , or  $\alpha$ -O-4 and  $\beta$ -O-4 linkages of lignin in supercritical ethanol at a high temperature. However, in the DL from the treatment with 50/50 (v/v) water-ethanol, the major identified compounds are almost exclusively monomeric phenolic and derivatives compounds (total relative area percentage of ~65 %). Typical compounds are 2-ethyl-5-propyl-phenol, diethyl-phenol, 2-ethyl-6-methylphenol, 2,6-bis(1-methylethyl)-phenol, and 1-isopropyl-2-methoxy-4-methylbenzen.

**Table 2- 2** GC-MS analysis of the depolymerized lignin, reprinted (adapted) with permission from ([Cheng et al.,2012](#)). Copyright Copyright © 2010 Elsevier

NO.	Ret. Time /min	Relative composition by area % <sup>1</sup>		Compound name
		50/50 (v/v) water-ethanol	pure ethanol	
a	3.660	4.10	- <sup>2</sup>	pentanoic acid, 3-methyl-
b	4.067	5.30	2.10	hexanoic acid
c	4.405	-	9.74	hexanoic acid, ethyl ester
d	4.501	-	1.56	2 (3H)-, dihydro- 4,5-dimethyl-furanone
e	4.798	-	3.54	1-hexanol, 2-ethyl-
f	4.925	3.13	-	benzenemethanol
g	4.989	-	2.30	2-hexensaeure, ethyl ester
h	5.343	-	4.55	1-octanol
i	5.879	-	5.98	hexanoic acid, 2-ethyl-, ethyl ester
j	6.288	-	2.40	phenol, 2,6-dimethyl-
k	6.426	1.87	2.78	benzenemethanol, 2-methyl-
l	6.649	-	3.34	nonanoic acid, ethyl ester
m	7.002	-	5.79	hexanoic acid, butyl ester
n	7.086	-	13.07	octanoic acid, ethyl ester
o	7.596	2.78	-	phenol, 3-ethyl-5-methyl-
p	7.700	1.67	-	phenol, 2-ethyl-5-methyl-

q	7.986	2.50	-	2-ethyl-6-methylphenol
r	8.127	-	1.63	1-decanol
s	8.289	-	2.19	phenol, 2-methyl-5-(1-methylethyl)
t	8.710	4.57	-	phenol, diethyl-
u	8.714	-	1.77	2-ethyl-4,5-dimethylphenol
v	8.854	1.78	-	phenol, 2,3,5,6-tetramethyl
w	9.200	6.68	4.11	phenol, 2-ethyl-5-propyl-
x	9.409	3.6	1.90	2-methoxy-4-(1-methylethyl) toluene
y	9.673	-	1.83	butyl octanoate
z	9.768	-	2.06	decanoic acid, ethyl ester
al	10.142	3.86	-	1-isopropyl-2-methoxy-4-methylbenzene
bl	10.204	5.71	1.61	phenol, 2,6-bis(1-methylethyl)-
cl	10.261	4.39	-	1,3-cyclohexadiene, 1,3,5,5,6,6-hexamethyl
d1	11.014	1.54	-	2-tert-butyl-1-methoxy-4-methylbenzene
e1	11.115	2.63	-	phenol, 3,5-bis(1-methylethyl)-
fl	11.358	2.16	-	2-methoxy-4-ethyl-6-methylphenol
gl	12.128	1.51	-	benzene, 1,2,4-triethyl-5-methyl
hl	12.213	1.57	-	3,4,5,6-tetraethyl-2h-pyran-2-one
il	12.722	3.50	-	benzene, 1,4-dimethoxy-2,3,5,6-tetramethyl-
gl	12.962	1.93	-	benzene, 1,3,5-tris(1-methylethyl)-
kl	17.741	1.65	-	1,1,3,3-tetramethyl-5,6-benz-2-indanone
ll	18.846	1.64	1.79	phenanthrene, 2,4,5,7-tetramethyl-
ml	20.260	1.87	-	dehydroabiatic acid
nl	21.328	2.38	-	1,2-benzendicarboxylic acid, dioctyl ester
Total area/%	74.32	76.04	-	-

<sup>1</sup>Total area was obtained based on the integration of 50 major peaks, without including the small peaks with an area % < 1.5%; <sup>2</sup>Not detectable.

The structure and functional group of DL products can be determined by means of Fourier transform infrared spectroscopy (FTIR), <sup>1</sup>H-NMR and <sup>13</sup>C-NMR. However, the FTIR results do not show big differences among DLs obtained at different reaction conditions but it did show differences in DLs from different types/sources of lignin ([El Mansouri et al, 2007](#)). <sup>1</sup>H-NMR and <sup>13</sup>C-NMR provide useful information of the distribution of different functional groups such as hydroxyl group and methoxy group. Comparison of <sup>1</sup>H-NMR peaks at 2.1 and 8.5 ppm for the DL and the original lignin, belonging to aliphatic and aromatic hydroxyl group, usually indicates the cleavage of ether linkages of the lignin ([Cheng et al., 2013](#)). The hydroxyl number can also be quantified with <sup>1</sup>H-NMR using internal standard such as dibromoethane ([Mahmood et al., 2013](#)). [Song et al.\(2013b\)](#) used the <sup>1</sup>H-NMR coupled with the deuterium isotopic tests to investigate the mechanism of lignin depolymerization. They found that the active

hydrogen species from alcohol instead of the presence of gaseous  $H_2$  plays a key role in lignin depolymerization.

## 2.6.3 Effects of process conditions

### *Type of Solvents*

Liquefaction of lignin or biomass in sub-/super-critical fluids such as water (Lawson and Klein, 1985; Benigni and Goldstein, 1971), methanol (Tsujino et al., 2003; Minami et al., 2003), and ethanol (Miller et al., 1999) has been studied by many researchers to obtain bio-oil products or phenolic chemicals with low molecular weights. Miller and co-workers (Miller et al., 1999) showed that supercritical ethanol was more reactive than methanol in the depolymerization of lignin and model compounds in a batch micro-reactor with base catalysts, resulting in less solid residual products. Cheng et al. (2010) also demonstrated that sub/supercritical ethanol was more reactive than methanol for liquefying woody biomass into oil products. The higher reactivity of ethanol than methanol might be owing to the slightly lower dielectric constant of ethanol (24.3 %) than that of methanol (33 %). As a result, ethanol in particular at its supercritical state may be expected to more readily dissolve and stabilize the relatively high molecular weight liquid products/intermediates derived from lignocellulosic biomass during the liquefaction/depolymerization process. Furthermore, Cheng et al. (2010) also showed that co-solvent of 50/50 (v/v) water-ethanol is much more reactive than either pure ethanol or water, leading to much higher biomass conversion and biocrude yields (up to 65 wt.%).

Effective depolymerization of kraft lignin was achieved by hydrothermal treatment in 50/50 (v/v) ethanol-water at 200 °C to 450 °C under 5 MPa  $H_2$  with or without catalyst (Cheng et al., 2012). The treatment at 300 °C for 2hr led to a yield of degraded lignin (DL, acetone-methanol soluble fraction) close to 90%. Molecular weights of the lignin were markedly reduced from its original  $M_w$  and  $M_n$  of 60,000 g/mol and 10,000 g/mol, respectively to ( $M_n$  415 g/mol,  $M_w$  1010 g/mol) for the DL. Compared with that in 50/50 (v/v) ethanol-water, treatment in pure ethanol led to a much lower yield of DL (< 15%) but the DL products have much smaller molecular weights ( $M_n$  260 g/mol and  $M_w$  631

g/mol in the 300 °C treatment). Moreover, the DLs from pure ethanol treatment are completely soluble in THF, compared with only ~30% solubility in tetrahydrofuran (THF) for the DLs from 50/50 (v/v) ethanol-water treatment.

### ***Reaction temperature and time***

Temperature plays a dominating role in lignin depolymerization. Extensive lignin depolymerization occurs only when temperature is increased sufficiently larger than the activation energies threshold for the chemical bond cessation. However, the effects of temperature are also bi-fold: a higher temperature could not only promote depolymerization of lignin, but also leads to the repolymerization of fragmented species. The competition between depolymerization and repolymerization defines the role of temperature of lignin depolymerization. At lower temperatures, depolymerization reactions dominate while increasing the reaction temperature, but the repolymerization reactions are promoted at higher temperatures resulting in formation of more char (solid residues). An intermediate temperature is usually the optimal temperature when the highest DL yield can be obtained. [Akhtar et al. \(2011\)](#) studied the process condition for HTL of biomass and reported that 300-350 °C is the best temperature range for biomass decomposition. [Yuan et al. \(2010\)](#) reported that 260 °C is the best temperature for NaOH-catalyzed hydrolytic lignin degradation process. The reaction temperature drastically influenced the DL product yields and properties: 300-350 °C appeared to be the optimal temperature for the process with 50/50 (v/v) ethanol-water ([Cheng et al., 2012](#)). In hydrolytic depolymerization of kraft lignin with NaOH catalyst, very high yield of DL (in the range of 85-92 wt.%) was obtained at 250-300 °C ([Mahmood et al., 2013](#)).

Reaction time is another important parameter for depolymerization of lignin. Duration of reaction time could affect the yield and composition of the DL products. Generally, secondary and tertiary reactions trigger for a prolonged reaction time. These reactions can break down the macromolecular into small fragmented molecules, gas or re-polymerized of the fragmented molecules into solid residues. Once the reaction has reached its saturated point at certain reaction time, increasing reaction time would result in decrease in DL yield. With respect to industrial scale, small residence time is usually preferred for

lignin depolymerization. [Yuan et al. \(2010\)](#) carried out the lignin depolymerisation in water-ethanol with NaOH as catalyst and phenol as capping agent at 260 °C in batch reactor from 0.5 to 2 h. They found that 1 h reaction time appeared to be the optimal reaction time for their system. Further increase in reaction time promotes the formation of solid residue due to repolymerization or cross linking of fragmented products. [Cheng et al. \(2012\)](#) reported that although the reaction time from 15 min to 360 min do not exhibit big difference in product yield and molecular weight distribution, 1-2 h reaction time was the optimal reaction condition for lignin depolymerization in water-ethanol co-solvent. Formic acid and alcohol mixtures have been found to be effective in decomposition of lignin, producing 25-35 wt.% phenolic oil yield at 380 °C, but a very long residence time (17 h) was needed. The produced DL products were found to have high H/C ratio of 1.66 and low O/C ratio of 0.17 ([Kleinert and Barth, 2008](#)).

### *Capping agents*

In lignin depolymerization, lignin is first decomposed in to smaller lignin species before further depolymerization or repolymerization reactions occurs. In order to avoid repolymerization of reactive species, capping agents, most commonly phenol proved to be effective ([Yuan et al., 2010](#)). [Nguyen et al. \(2014\)](#) studied the lignin depolymerization using base catalyst  $K_2CO_3$  and also phenol as capping agent in a continuous-flow fixed-bed reactor. The oxygen content in the oil phase was found to be reduced by 10 wt.% along with an increased heating value (HHV of the DL attained 32 MJ/kg). The 1-ring aromatics compounds produced were increased from 17 to 28 wt.% by the addition of  $K_2CO_3$ . [Toledano et al. \(2014\)](#) investigated two capping agents, phenol and boric acid, on improving base catalyzed lignin depolymerization by avoiding lignin repolymerization. Phenol capping agent was found to favor production of phenolic compounds while boric acid capping agent increased char formation

## 2.7 Reductive depolymerization of lignin

Reductive depolymerization of lignin is achieved by cleaving the ether bonds present in the lignin molecules with hydrogen molecules or atoms. In this process, an organic

solvent and a supported catalyst (such as expensive carbon-supported Pt or Ru catalysts) is needed (Yan et al., 2008). The reactive hydrogen could be obtained from gaseous hydrogen in combination with suitable catalysts or a solvent medium. From the report by Yan et al. (2008), wood lignin (using pine and birch sawdust as the lignin source) could be effectively degraded into monomers of guaiacylpropane, guaiacylpropanol, syringylpropane and syringylpropanol in hot-compressed water at 200 °C for 4 h under 4 MPa (cold pressure) H<sub>2</sub> with carbon-supported Pt or Ru catalysts, where the biomass-to-solvent ratio was fixed at about 1:15 (wt/wt). The yield of total mono-phenols was as high as 45 % of the total amount of C<sub>9</sub> units in the lignin when co-solvent of dioxane/H<sub>2</sub>O (1:1 wt/wt) with 1 H<sub>3</sub>PO<sub>4</sub> (1 wt.% of the solvent) was used combined with Pt/C catalyst (5 wt.% of the sawdust). In a recent work by Cheng et al. (2012), effective depolymerization of kraft lignin was achieved by hydrothermal treatment in 50/50 (v/v) ethanol-water at 200 °C to 450 °C under 5 MPa H<sub>2</sub> with or without catalyst of alumina or activated carbon supported metal catalysts (Pt, Ru, Ni). The treatment at 300 °C for 2hr led to a yield of degraded lignin (DL, acetone-methanol soluble fraction) close to 90%. Molecular weights of the lignin were markedly reduced from its original M<sub>w</sub> and M<sub>n</sub> of 60,000 g/mol and 10,000 g/mol, respectively to (M<sub>n</sub> 415 g/mol, M<sub>w</sub> 1010 g/mol) for the DL. The use of alumina or activated carbon supported metal catalysts (Pt, Ru, Ni) did not affect the yields of DL, but it could slightly reduce the molecular weights of the DLs and greatly increased the solubility of DLs in THF, particularly in the process with 50/50 (v/v) ethanol-water.

### 2.7.1 Effects of catalysts

The most common catalyst types in reductive depolymerization of lignin are supported metals. The performances of various supported metals catalysts in reductive lignin depolymerization are summarized in Table 2-3.

From the results outlined in Table 2-3, some key conclusions may be drawn as follows:

- (1) Ru<sub>5%</sub>/C as the commercial catalyst is highly effective for reductive lignin depolymerization. With Ru<sub>5%</sub>/C catalyst, kraft lignin was converted into DL at >75 wt.%

yield at 400 °C for 4 h reaction. Model compound studies using PPE showed that Ru<sub>5%</sub>/C was effective in hydrogenation of benzene rings rather than C-O bond cleavage that lead to low yield of degraded lignin.

- (2) Ru is an expensive noble metal, some inexpensive metals (Ni, Mo, etc) catalysts are more attractive for industrial applications. For instance, with Ni<sub>10%</sub>/AC, organosolv lignin was converted into DL at 91.4 wt.% yield and an  $M_w$  of 1137 g/mol at 300 °C for-2 h. With CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst, conversion of 84 wt.% for guaiacol was achieved with 36 % selectivity towards phenol at 300 °C for 4 h.
- (3) Ni-based catalyst was demonstrated to be effective for producing lower molecular weight lignin oligomers and bio-oils from lignin. 85 wt.% conversion of phenethyl phenyl ether (PPE) into phenol and ethyl cyclohexane was realized at a low temperature 150 °C for 2 h under 2 MPa hydrogen pressure, and Birch lignin was successfully converted into DL at 42 wt.% yield with  $M_w$  of 1409 g/mol when Ni/C catalyst was applied.
- (4) Supported catalysts based on CuO, Pt and CuLa were also found to be active in converting lignin into hydrogenated products or low molecular weight degraded products under reductive condition. 17.3 wt.% phenol was produced from ethyl acetate using CuO/Al<sub>2</sub>O<sub>3</sub> while 97 wt.% propylcyclohexane was obtained from 4-propyl-phenol using Pt/AC catalyst.



**Table 2- 3** Performances of various supported metals catalysts in reductive lignin depolymerization

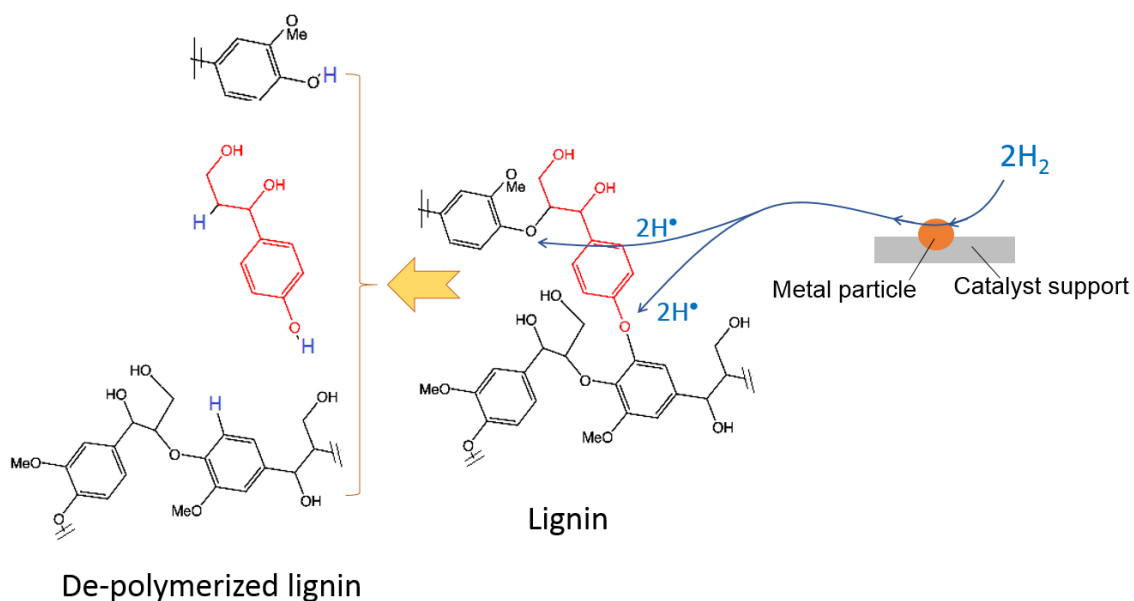
Catalysts	Lignin or model compound type and amount	Initial H <sub>2</sub> Pressure (MPa)	Optimal reactions conditions (solvent type, temp., time, etc.)	Yields (DL, SR or Major compound) at optimal conditions	M <sub>w</sub> of DL at optimal conditions (g/mol)	References
Ru <sub>5</sub> %/C	Pyrolytic lignins, 15 g	10	400 °C, 4 h	>75 wt.% DL <sup>1</sup>	-	<a href="#">Kloekhorst et al. (2014)</a>
Ru <sub>5</sub> %/C	Phenethyl phenyl ether (PPE), 0.167 mol	2	150 °C, 2 h	100 wt.% hydrogenated products (19 % cyclohexanol 21 % ethyl cyclohexane 60% hydrogenated PPE)	-	<a href="#">Song et al. (2013a)</a>
Ni/C	Phenethyl phenyl ether, 0.167 mol	2	150 °C, 2 h	85 wt.% (phenol and ethyl cyclohexane)	-	<a href="#">Song et al. (2013a)</a>
Ni <sub>10</sub> %/AC	Organosolv lignin, 1g	5	10 ml 50/50 water-ethanol (v/v), 300 °C, 2 h	91.4 wt.% DL <sup>1</sup>	1137	<a href="#">Cheng et al. (2013)</a>
Ru <sub>10</sub> %/Al <sub>2</sub> O <sub>3</sub>	Organosolv lignin, 1g	5	10 ml 50/50 water-ethanol (v/v), 300 °C, 2 h	92.1 wt.% DL <sup>1</sup>	1193	<a href="#">Cheng et al. (2013)</a>
NiMo/Al <sub>2</sub> O <sub>3</sub>	Wheat straw soda lignin, 30 g	3.7	70 g tetralin and 16 µL DMDS, 350 °C, 5 h	64 wt.% DL <sup>1</sup>	4915	<a href="#">Joffres et al. (2014)</a>
CuLaPMO	Organosolv lignin (M <sub>w</sub> 2449 g/mol), 100 mg	-	3 ml methanol, 1 h	42.7 wt.% DL <sup>2</sup>	474	<a href="#">Warner et al. (2014)</a>
Ni/HTC	Clean fractionation (CF) lignin (300-10000 Da)	-	MIBK, 270 °C, 1 h	-	200-2000 Da	<a href="#">Sturgeon et al. (2014)</a>
α-MoC <sub>1-x</sub> /AC	Kraft lignin	10.5	Ethanol, 280 °C, 6 h	1.64 g abundant liquid products per gram of ligni	700-1400	<a href="#">Ma et al. (2014)</a>
Raney Nickel	Enzymolysis lignin, 300 mg	2	20 ml 3% NaOH in dioxane/H <sub>2</sub> O, 180 °C, 3.5 h	82.3 wt.% DL <sup>3</sup>	1368	<a href="#">Xin et al. (2014)</a>
CoMo/Al <sub>2</sub> O <sub>3</sub>	Guaiacol, 1.5 g	5	30 g dodecane, 300 °C, 4 h	84 wt.% conversion (selectivity 36 % towards phenol )	-	<a href="#">Jongorius et al. (2012)</a>
Ni/HZSM-5	Benzyl phenyl ether 0.01 mol	4	80 ml water, 250 °C, 240 min	50 % phenol and 40 % toluene	-	<a href="#">He et al. (2014)</a>
Ni/SiO <sub>2</sub>	Benzyl phenyl ether 9.2 g	4	80 ml water, 250 °C, 110 min	50 % phenol and 50 % toluene	-	<a href="#">He et al. (2014)</a>
Ru/SiO <sub>2</sub> -	Guaiacol, 0.5475 g	4	40 ml n-decane, 250 °C, 1	60 mol% cyclohexane	-	<a href="#">Lee et al. (2012)</a>

Al <sub>2</sub> O <sub>3</sub>			h			
Pt/AC	4-propyl-phenol, 272 mg	4	40 ml water, 280 °C, 1 h	97 wt.% propylcyclohexane	-	<a href="#">Ohta et al. (2014)</a>
Ni/C	Birch lignin, 2.0 g	5	40 ml methanol, 200 °C, 6 h	42 wt.% DL <sup>2</sup>	1309	<a href="#">Song et al. (2013b)</a>
CuO/Al <sub>2</sub> O <sub>3</sub>	2-phenoxy-1-phenylethanone 0.12 mg	2.5	10 ml ethyl acetate, 150 °C, 21 h	96.7 wt. conversion (17.3 wt.% phenol)	-	<a href="#">Strassberger et al. (2013)</a>
NiAu	2-phenoxy-1-phenylethanol 0.22 mmol	1	3 ml water, 130 °C, 2.5 h	87 wt.% monomer	-	<a href="#">Zhang et al. (2014)</a>

<sup>1</sup> Acetone-soluble <sup>2</sup> Methanol-soluble <sup>3</sup> Precipitation by HCl solution

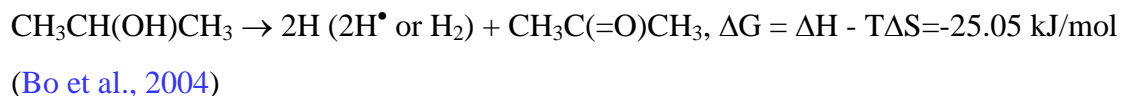
## 2.7.2 Effects of hydrogen source

Reductive lignin depolymerization is mostly carried out in hydrogen gas atmosphere in combination with a supported metal catalyst and a suitable solvent such as alcohol and acetone, as described in Table 2-3. At elevated temperatures, the  $H_2$  would diffuse from the gas phase into the solvent and get adsorbed by the metal followed by dissociation into hydrogen atom or radical ( $H$  or  $H^\bullet$ ) on the metal particle surface. The  $H^\bullet$  radicals would move into the lignin structure and cleave lignin's ether linkage to de-polymerize macromolecules into monomers and oligomers. This possible reaction mechanism of reductive depolymerization of lignin is illustrated in Figure 2-3,



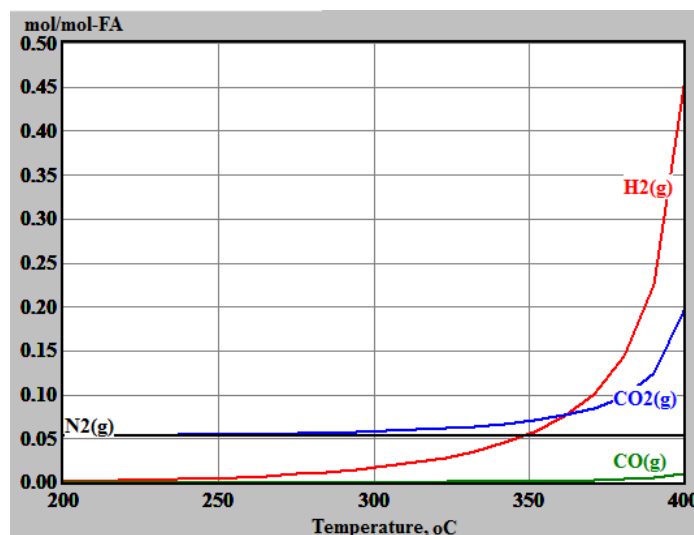
**Figure 2-3.** Possible reaction mechanism of reductive depolymerization of lignin

Instead of using external  $H_2$  gas, there is internal or in-situ hydrogen source coming from decomposition of solvents such as formic acid and 2-propanol that are less thermally stable and will decompose to give hydrogen atom (or radicals or  $H_2$ ) and  $CO_2$  and acetone, respectively, upon heating at elevated temperatures, as shown below.



Recently, hydrogen-donating solvents have found special applications in reductive depolymerization of lignin. As reported by Kleinert et al. (Kleinert and Barth, 2007; Kleinert and Barth, 2008, 2008a; Kleinert et al., 2009; Kleinert and Barth, 2011), formic acid and 2-propanol were used as hydrogen donors to de-polymerize and hydrogenate lignin. Reductive depolymerization/hydrogenation of lignin in formic acid (and ethanol as a co-solvent) and 2-propanol that generates *in-situ* hydrogen was demonstrated, although the yields of DL products or phenolic oil were low, being only 25 – 35 wt.% at 380 °C and a very long residence time (8-54 h). Nevertheless, the DL products were exclusively composed of monoaromatic phenols with alkylation ranging from C<sub>1</sub>–C<sub>7</sub> in the side chain(s), and the yield was 2 or 3 times that of earlier work by Dorrestijn et al. (1999) using AnH<sub>2</sub> for depolymerization of wood lignin at 352 °C.

Formic acid (FA) and 2-propanol can decompose to form *in-situ* hydrogen gas (hydrogen atoms or radicals) at elevated temperatures above approx. above 200°C, as evidenced by thermodynamics calculation for a batch reactor system under conditions of formic FA-to-lignin mass ratio of 0.7, ethanol-water co-solvent (50/50, v/v), 1 h, 300 °C, 2 MPa initial N<sub>2</sub> pressure (Figure 2-4).



**Figure 2- 4** Equilibrium yields of gaseous species, calculated using HSC 5.1 software for the reaction system under the conditions of (FA-to-lignin mass ratio of 0.7, ethanol-water co-solvent (50/50, v/v), 1 h, 300 °C, 2 MPa initial N<sub>2</sub> pressure)

In a recent work by [Cheng \(2011\)](#), formic acid that can act as a hydrogen donor at elevated temperatures was employed for depolymerization of alkali lignin (AL) or kraft lignin (KL) and organosolv lignin (OL) in the medium of sub-/super-critical 50/50 (v/v) water-ethanol. The obtained DL products were further analyzed by gel permeation chromatography (GPC) and proton nuclear magnetic resonance (<sup>1</sup>H NMR). The depolymerization of AL and OL led to 77 wt% and 80 wt% yield of DL, and 5 wt% and 0.4 wt% yield of solid residue (SR), respectively. The relative molecular weights of the DL products were significantly decreased compared to those of the original lignin samples. For instance, M<sub>n</sub> of the AL reduced from 10,000 to 295 g/mol, while the M<sub>n</sub> of the OL decreased from 307 g/mol to 150 g/mol. The <sup>1</sup>H NMR analysis of DL demonstrated that the methoxyl groups were significantly decreased after degradation in formic acid compared to the original lignin samples. The use of formic acid was found to be effective for increasing the DL yields while suppressing the formation of solid residues compared with the use of gaseous hydrogen, likely because the in situ formed hydrogen atoms (radicals) have higher mobility to lignin structure, even without the presence of a supported metal catalyst.

## 2.8 Summary and conclusions

(1) Lignin can be an abundant natural source of aromatics (bio-phenolic chemicals or bio-polyols) after liquefaction or depolymerization.

(2) Degraded/depolymerized lignins are more chemically reactive for the synthesis of bio-based phenolic resins, polyurethane resins and epoxy resins, as they have a smaller molecular weight, less steric hindrance effects and more active functional groups.

(3) Many technologies, such as pyrolysis and HTL or hydrolytic depolymerization have been applied to liquefy (or de-polymerize) lignin into phenolic oils or depolymerized lignin. The oil yields are quite low in lignin pyrolysis processes, leaving a large amount of char. In contrast, HTL or hydrolytic depolymerization technology provides various benefits that are unparalleled in comparison with other technologies such as gasification, wet oxidation and pyrolysis.

(4) The hydrolytic depolymerization mechanism involves cleaving of mainly the  $\beta$ -O-4 ether bond under base or water condition, accompanied with dealkylation of side chains and hydrolysis of methoxyl groups.

(5) Depolymerization of lignin can be effectively achieved by cleaving the ether bonds present in the lignin molecules with hydrogen molecules or atoms – so called reductive depolymerization. In this process, an organic solvent and a supported catalyst (such as expensive carbon-supported Pt or Ru catalysts) is needed.

(6) The reactive hydrogen could be obtained from gaseous hydrogen in combination with suitable supported metal catalysts and a solvent medium, or from an internal or in-situ hydrogen source coming from decomposition of solvents such as formic acid and 2-propanol upon heating at elevated temperatures.

(7) The use of formic acid was found to be effective for increasing the DL yields while suppressing the formation of solid residues compared with the use of gaseous hydrogen, likely because the in situ formed hydrogen atoms (radicals) have higher mobility to lignin structure, even without the presence of a supported metal catalyst.

This thesis reports a comprehensive study on the effects of formic acid as an internal (in-situ) hydrogen source without (Chapter 3) and with supported metal catalysts (Chapter 4) on reductive depolymerization of kraft lignin. The work of Chapter 3 mainly focused on optimization of lignin reductive depolymerization using formic acid, while the work of Chapter 4 focused on catalyst screening in order to lowering the reaction temperature and pressure to facilitate industrial application of the kraft lignin reductive depolymerization with formic acid.

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## Chapter 3 Reductive Depolymerization of Kraft Lignin for Chemicals and Fuels using Formic Acid as an *In-situ* Hydrogen Source

### 3.1 Introduction

Utilization of lignocellulosic biomass for the production of chemicals and fuels has attracted growing attention as it does not compete with food production. In lignocellulosic biomass, while cellulose has been used for sugar/ethanol production and pulp/paper manufacture, lignin is generated as a by-product (15-30 % by weight, 40 % by energy) that is used as mainly a fuel for heat and power generation ([Perlack et al., 2005](#)).

According to the International Lignin Institute, the annual production of kraft lignin (KL) in the form of “black liquor” exceeds 40-50 million tons, which is combusted in recovery boilers to supply a majority of the energy requirement for a pulp/paper mill. However, in North America, more than 65% of pulp/paper mills have an operation bottleneck in the capacity of recovery boilers. This provides great opportunities for the utilization of KL, separated from the “black liquor”, for other applications such as bio-fuels, bio-chemicals and biomaterials, which would help to diversify the revenue for pulp and paper mills.

Lignin is an amorphous polymer comprised of three phenyl-propanols i.e., p-hydroxyl-phenyl propanol, guaiacyl-propanol and syringyl-propanol, via condensed linkage (e.g., 5-5,  $\beta$ - $\beta$ ,  $\beta$ -5 and  $\beta$ -1 linkages) and primarily ether linkages (e.g.,  $\alpha$ -O-4, 5-O-4 and  $\beta$ -O-4). Lignin thus has great potential as precursors for aromatic (phenolic) chemicals for sustainable production of various bio-based chemicals and materials such as adhesives, polyurethane foams, flocculants and epoxy coating ([Khitrin et al., 2012](#)).

However, the lower reactivity and high steric hindrance effect, caused by its large molecular weight and branched structure, limits the direct use of lignin for replacement of petroleum based chemicals. One way to enhance reactivity of lignin is to modify the chemical structure of lignin, e.g., phenolation or methylation of lignin (reacting lignin with phenol or formaldehyde) could improve the reactivity of lignin in the synthesis of lignin-based phenol formaldehyde resins ([Clarke et al., 1978](#)). The other more effective

approach is to de-polymerize lignin into oligomers with smaller molecules (Thring, 1994). Using depolymerized lignin, bio-phenol-formaldehyde (BPF) resins of a phenol substitution ratio up to 75-90% was successfully produced in our lab, and the plywood specimen glued by the BPF adhesives have stronger or comparable shear strength than those with pure PF adhesive (Cheng et al., 2013).

Lignin depolymerization methods mainly include biological method using enzyme and thermal method using heat (such as pyrolysis) and thermochemical methods using heat and chemicals, such as hydrolytic depolymerization using water and alkaline catalyst and reductive depolymerization using hydrogen. Among those methods, biological process is a very slow process, while pyrolysis operated at 400-800°C is fast, but lignin pyrolysis resulted in a low oil product yield (20-40 wt.%) with high energy consumption in particular for wet feedstocks (Pandey et al., 2008). In contrast, hydrolytic depolymerization of lignin operates under milder conditions requiring moderate temperatures (200-300°C) but higher pressures (50-150 bar). Hydrolytic depolymerization of lignin can be realized through the hydrolytically cleavage of ether bonds in lignin catalyzed by an acid or base catalyst (Fang et al., 2008). For example, hydrolytic depolymerization of lignin was conducted at low temperatures in the presence of sulfuric acid, but the main drawback is that repolymerization of degraded intermediates resulted in a high yield of solid residue (Matsushita and Yasuda, 2005). Kraft lignin (KL) was successfully depolymerized into oligomers with moderately low weight-average molecular weight ( $M_w$  of 1000-3000 g/mol) via direct hydrolysis using NaOH as a catalyst, without any organic solvent/capping agent (Mahmood et al., 2013) or with phenol as a capping agent (Yuan et al., 2010).

Reductive depolymerization of lignin is achieved by cleaving the ether bonds present in the lignin molecules with hydrogen molecules or atoms. In this process, an organic solvent and a supported catalyst (such as expensive carbon-supported Pt or Ru catalysts) is needed (Yan et al., 2008). Formic acid and 2-propanol can decompose to form *in-situ* hydrogen gas at elevated temperatures above approx. above 200°C. Reductive depolymerization/hydrogenation of lignin in formic acid (and ethanol as a co-solvent) and 2-propanol that generates *in-situ* hydrogen was also demonstrated (Kleinert and

Barth, 2008a,b; Kleinert et al., 2009), although the yields of phenolic oil were low, being only 25–35 wt.% at 380 °C and a very long residence time (8–54 h).

In recent thesis work by Cheng from the authors' group (Cheng, 2011), formic acid was employed in the depolymerization of alkali lignin (AL) and organosolv lignin (OL) in a water-ethanol (50/50, v/v) medium at 300–350 °C, obtaining 70–80% DL yields. The use of formic acid was found to be more effective in increasing the DL yields while also suppressing the formation of solid residues as compared with the use of gaseous hydrogen, likely because the in situ formed hydrogen from formic acid can prevent the recombination of reaction intermediates. It has been proven that the use of ethanol-water co-solvent has synergistic effects on hydrothermal liquefaction of woody biomass (Cheng et al., 2010), which might partially contribute to the high yield of DL in the lignin depolymerization process.

Continuing the work of Cheng (2011), this work presents a systematic study on the reductive depolymerization of kraft lignin acid in ethanol-water and as co-solvent with formic acid under various conditions (temperature, pressure, reaction time, and ethanol concentration in the ethanol-water reaction media). The gas composition was analyzed by Micro-GC. The DL products were analyzed by elemental analysis, Gel Permeation Chromatography (GPC), Fourier Transform Infrared Spectroscopy (FT-IR) and  $^1\text{H}$  NMR.

## 3.2 Materials and Methods

### 3.2.1 Materials

Kraft lignin (KL) was provided by FP Innovations, with  $M_w$  and  $M_n$  of  $\approx 10,000$  g/mol and  $\approx 5,000$  g/mol, respectively, as determined by GPC-UV. The dried sample of KL contains 0.57 wt.% ash and 1.52 wt.% sulfur (on a dry-and-ash-free basis). In this study, ACS reagent grade solvents and chemicals including ethanol, acetone, formic acid (FA) (>95 %) were used. HPLC grade tetrahydrofuran (THF) containing 0.03 wt.% 2, 6-di-*t*-butyl-4-methyl-phenol stabilizer was used in the GPC analysis for the depolymerized lignin (DL) products.

### 3.2.2 Depolymerization of kraft lignin

The depolymerization of KL was performed in a 100 mL Parr reactor with maximum working pressure of 34 MPa at 600 °C. In a typical run, 5.0 g KL, 3 mL amount of formic acid (FA) and 30 mL water/ethanol (1:1 v/v) were loaded into the reactor. The reactor was sealed, evacuated and purged three times with N<sub>2</sub> followed by pressurizing the reactor to 2 MPa with N<sub>2</sub>. The reactor was heated to the specified temperature for a specified time while stirring at 200 rpm. After the predetermined reaction time had elapsed, the reactor was quenched in a water bath to stop the reaction. The resulted gaseous products were collected in a gas bag with injection of 500 mL of air as an internal standard and analyzed for gas composition (H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>-C<sub>3</sub>) with a Micro-GC-TCD. The remaining reaction products were rinsed from the reactor with acetone followed by vacuum filtration through a preweighed filter paper. The acetone-soluble fraction was isolated by rotary evaporation under reduced pressure at 40-60 °C to remove the organic solvents and residual water. The resulting liquid phase after evaporation was designated depolymerized lignin (DL), and was vacuum dried at room temperature overnight before weighing. The residue after filtration was oven dried at 105 °C for 24 h to obtain the weight of the solid residue (SR). The yields of DL and SR are calculated as follows:

$$\text{DL (wt.\%)} = \frac{W_{\text{DL}}}{W_{\text{KL}}} \times 100\% \quad (1)$$

$$\text{SR (wt.\%)} = \frac{W_{\text{SR}}}{W_{\text{KL}}} \times 100\% \quad (2)$$

Where  $W_{\text{DL}}$  is the weight of the acetone-soluble DL,  $W_{\text{KL}}$  the weight of the dried KL and  $W_{\text{SR}}$  the weight of the obtained dried SR.

Different temperatures, pressures, reaction times and proportions of FA and water-ethanol co-solvent or other solvents were investigated to study the effects of these reaction parameters on the reductive depolymerization of kraft lignin. At least 2-3 runs were performed to ensure the reproducibility of the products yields (with relative errors

in DL and SR yields within 10% between all the replicate runs). The results reported in this work are mostly the average of values from replicate runs.

### 3.2.3 Characterization of reaction products

As described previously, the gaseous products, collected in a gas bag, were analyzed by GC-TCD. The DL products were subject to more comprehensive analyses, i.e., molecular weights and distributions, elemental analysis and proton nuclear magnetic resonance ( $^1\text{H}$ -NMR).

Molecular weights and distributions of the DL products were determined using a Waters Breeze gel permeation chromatography (GPC) instrument [1525 binary high-performance liquid chromatography (HPLC) pump; UV detector at 270 nm; Waters Styragel HR1 column at 40 °C] with THF as the eluent at a flow rate of 1mL/min. Polystyrene standards were used for calibration

The elemental analysis was employed to investigate the C, H, O and S composition of the obtained DLs on a Thermo Fischer Flash EA 1112 series CHNS-O elemental analyzer. The results of elemental analysis were used to calculate H/C and O/C ratios of the DL products.

Proton nuclear magnetic resonance ( $^1\text{H}$ -NMR) spectra for DLs were acquired at room temperature on Varian Inova 600 NMR spectrometer equipped with a Varian 5mm triple-resonance indirect-detection HCX probe. A total of 16-32 scans were accumulated using a 2s recycle delay, 3.6s acquisition time, a 45-degree tip angle ( $p_w = 4.8$  us), and a spectral width from -2 ppm to 14 ppm ( $sw = 9000.9$  Hz).  $d_6$ -DMSO and  $d$ -chloroform were used as the solvents for qualitative  $^1\text{H}$ -NMR study. Quantitative  $^1\text{H}$ -NMR analysis was conducted using acetylated samples of the KL and DLs, prepared following the procedures detailed elsewhere (Mahmood et al., 2013). The resulting acetylated KL/DLs samples were then dried at 105 °C for 24 hr to remove residual water. Dibromomethane ( $\text{CH}_2\text{Br}_2$ ) was chosen as an internal standard and the solvent selected for the quantitative analysis was  $d$ -chloroform. For determining hydroxyl number through  $^1\text{H}$ -NMR, the samples were prepared by first weighing 15 mg of the acetylated KL or DL and 10 mg of

internal standard in a vial and then the sample was transferred into a 5 mm NMR tube via a transfer pipette using *d*-chloroform ( $\approx 1000$ -1500 mg) for the subsequent  $^1\text{H}$ -NMR measurements.

The detail distribution of the degraded lignin will not be determined as the similar results were reported in [Cheng et al.\(2012\)](#). Moreover, due to the complexity of degraded products, not all of them can be detected by Gas Chromatography- Mass Spectrometry (GC-MS) as some compounds have higher boiling point and cannot be vaporized or may decomposed into other compounds at high temperature.

### 3.3 Results

The KL products obtained were in the form of a black viscous liquid, and soluble in organic solvents such as THF and acetone, which facilitated molecular weight and distribution analysis. In general, the DLs obtained from this study have number-average molecular weight ( $M_n$ ) and weight-average molecular weight ( $M_w$ ) values of 150-600 g/mol and 500-3200 g/mol, respectively, largely dependent on the reaction parameters, i.e. FA-to-lignin mass ratio, solvent composition, reaction time, reaction temperature, substrate concentration, etc. The effects of these reaction parameters on the yields and molecular weights and distributions of the DL products are discussed as follows.

#### 3.3.1 Effects of FA-to-lignin mass ratios

The effects of varying mass ratios of FA to KL on lignin depolymerization were studied using at 300 °C for 1 h using 5 g KL, 30 mL water-ethanol co-solvent (50/50 v/v) and 0-10 mL formic acid. Table 3-1 presents the yields of DL and SR at varying FA-to-lignin mass ratios (w/w). All DLs obtained are soluble in acetone. As shown in Table 3-1, operations at the FA-to-lignin mass ratio of 0.2-2.4 produced highest high DL yield (84-89 wt.%) and lowest solid residue (0.5-2.5 wt.%), as compared to DL and SR yields of 71.5 and 15.8 wt.%, respectively, without the addition of FA. These results show that the addition of FA enhanced kraft lignin depolymerization.

**Table 3- 1** Effects of FA-to-lignin mass ratio on the products yield and molecular weights and distribution of DL

FA-to-KL ratio(w/w)	Yield (wt.%)		GPC results of DLs			Operating pressure (MPa)
	DL	SR	M <sub>n</sub> (g/mol)	M <sub>w</sub> (g/mol)	PDI (M <sub>w</sub> /M <sub>n</sub> )	
lignin	-	-	5,000	10,000	2.0	-
0.0	71.5(±0.4)	15.8(±0.6)	460	2000	6.6	11.0-12.0
0.2	84.2(±0.4)	2.0(±0.6)	460	1450	3.2	11.7-12.0
0.7	88.0(±2.7)	0.5 (±0.2)	410	1270	3.1	12.0-12.4
1.5	87.6(±0.1)	0.9(±0.2)	470	1320	2.8	14.0-17.2
2.4	86.7(±0.2)	2.5 (±1.4)	500	1270	2.6	14.5-24.1

Note: Other reaction conditions are water-ethanol co-solvent (50:50 v/v), 300 °C, 1 h.

The DL products were analyzed on a GPC to determine their relative molecular weights. Table 3-1 presents number-average (M<sub>n</sub>), weight-average (M<sub>w</sub>) molecular weights and poly-dispersity index (PDI = M<sub>w</sub>/M<sub>n</sub>) of the DL products, along with the yields of DL and SR from experiments in water-ethanol co-solvent (50:50 v/v) at 300 °C for 1 h with various FA-to-lignin mass ratios. Based on the M<sub>w</sub> values listed in the Table 3-1, it is clear that the presence of FA led to decreases in both molecular weights and PDI of the DL products, accompanied by an increase in DL yield and reduction in SR. This is likely due to the hydrogen donation effects of formic acid and the suppression of repolymerization reactions involving the reactive intermediates from degraded lignin, as discussed later. As a general trend, a higher FA-to-lignin mass ratio produces a DL of a lower M<sub>w</sub> and a smaller PDI. The lowest M<sub>w</sub> (1270 g/mol) and the smallest PDI (2.6) were attained at a FA-to-lignin mass ratio of 0.7 or 2.4 and 2.4, respectively. Compared with the M<sub>w</sub> of ~10,000 g/mol for the original lignin, this process employing a water-ethanol co-solvent and formic acid proved to be very effective for depolymerization of

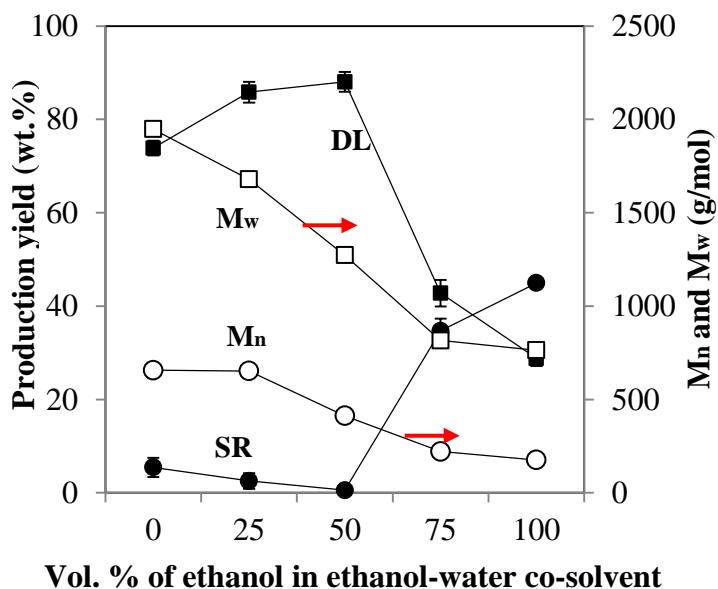
KL into lower molecular weight aliphatic and aromatic products that can be utilized as replacement chemicals for phenols and polyols in various bioproducts (resins, adhesives and foam materials). However, the results in Table 3-1 show that both  $M_n$  and  $M_w$  level off at the FA-to-lignin mass ratio of 0.7 and actually increase slightly when further increasing the FA-to-lignin mass ratio. This can likely be attributed to the difficulty in cleaving of the C-C linkages in KL and the increased acidity at a higher FA-to-lignin mass ratio that could lead to condensation/repolymerization of the reaction intermediates (Gosselink et al., 2012). The above results suggest that FA-to-lignin mass ratio at around 0.7 (corresponding to 3 mL FA for 5.0 g KL) may be optimal for KL depolymerization.

### 3.3.2 Effects of solvent composition

Alcohol-water co-solvents, and 50/50 (v/v) co-solvent systems in particular, proved to be more efficient solvents than either pure alcohol or water for the hydro-/hydrothermal liquefaction of a woody biomass owing to the synergistic effects of alcohol (diluting the reaction intermediates to prevent repolymerization) and water (to promote hydrolytic depolymerization of lignin) (Xu and Etcheverry, 2008; Cheng et al., 2010; Cheng et al., 2012). It is thus of interest to investigate the effects of alcohol-water co-solvent on the reductive degradation of KL using formic acid as an *in-situ* hydrogen source. In this study, KL was treated in an ethanol-water co-solvent of various ethanol volume fractions (0-100 vol.%) at 300 °C for 1 h at an FA-to-lignin mass ratio of 0.7. Figure 3-1 represents the effects of ethanol volume fraction in water-ethanol co-solvent on the yields of DL and SR in the KL depolymerization process. The results revealed that an ethanol content of 50% (v/v) in the co-solvent system produced the maximum DL yield (~ 90 wt.%) and the lowest SR yield (< 1 wt.%), which is in good agreement with the results of the previous studies on the hydrothermal liquefaction of biomass (Cheng et al., 2010; Cheng et al., 2012). As the ethanol content in the co-solvent system increased to > 50% (v/v), the DL yield decreased, accompanied by a drastic increase in SR yield, which may be related to a decreasing effect of hydrolytic depolymerization (Akiya, 1998). As such, with respect to DL yield, the 50/50 (v/v) co-solvent of ethanol-water was found to be the most effective solvent for reductive depolymerization of KL. With respect to the molecular weights of the DL products, in general, both  $M_w$  and  $M_n$  decrease with increasing ethanol content in



the ethanol-water co-solvent system, as clearly displayed in Figure 3-1. This might be accounted for by the diluting effects of alcohol which could effectively prevent repolymerization of the reaction intermediates, resulting in DL products of a lower  $M_w$  or  $M_n$ .



**Figure 3- 1** Effects of ethanol volume fraction in water-ethanol co-solvent on the DL and SR yields and molecular weights of DLs (other reaction conditions: 300 °C, 1 h, FA-to-lignin mass ratio of 0.7)

### 3.3.3 Effects of reaction time

Effects of reaction time on the yields of DL and SR in depolymerization of kraft lignin in water-ethanol co-solvent (50/50 v/v) at 300 °C for 0.5-2 h at an FA-to-lignin mass ratio of 0.7 are displayed in Table 3-2. As seen in Table 3-2, the effects of reaction time on the yields of DL and SR were minimal: e.g., while the reaction time ranged from 0.5 h to 2 h, the yields of DL were in the narrow range of 87.1-89.1 wt.%. Table 3-2 also presents the average molecular weights and distribution of the DLs obtained from operations for different lengths of time. Generally, as shown in Table 3-2, the weight average molecular weight ( $M_w$ ) decreases continuously from the  $M_w$  1550 to 1040 g/mol. A longer residence

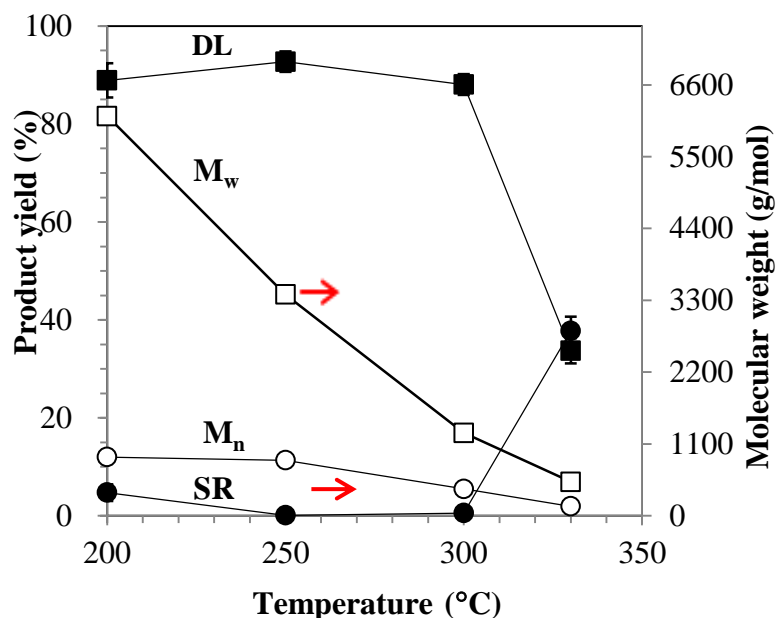
time thus promotes KL depolymerization to yield a DL of a lower  $M_w$ , as was similarly observed by [Cheng et al. \(2012\)](#). From Table 3-2., the reaction time of 0.5-1 h appears to be optimal with approx. 90 wt.% DL yields and negligibly small yields of solid residue (0.5 wt.%). It was also found that the decreasing trend of  $M_w$  with prolonged reaction time leveled off after 1 h. Reaction time longer than 2 h is not economically desirable and repolymerization of the lignin-derived intermediates could occur, leading to reduced yields of DL products with an increased  $M_w$  ([Xu et al., 2012](#)). Hence, all KL depolymerization operations in this study were performed for a time not longer than 2 h.

**Table 3- 2** Effects of reaction time on the yields and GPC results of DL and SR [water-ethanol co-solvent (50:50 v/v), 300 °C, FA-to-lignin mass ratio of 0.7]

Reaction time (h)	Yield (wt.%)		GPC results of DLs		
	DL	SR	$M_n$ g/mol	$M_w$ g/mol	PDI
lignin	-	-	5,000	10,000	2.0
0.5	89.1(±0.9)	0.5 (±0.2)	490	1550	3.2
1	88.0(±2.8)	0.5 (±0.2)	410	1270	3.1
2	87.1(±0.6)	0.3(±0.3)	390	1040	2.6

### 3.3.4 Effects of reaction temperature

Figure 3-2 shows the dependency of DL and SR yields on reaction temperature. The effects of reaction temperature were studied from 200 to 330 °C at a constant reaction time (1 h) and a fixed FA-to-lignin mass ratio of 0.7.



**Figure 3- 2** Effect of temperature on product yields (Other reaction conditions: water-ethanol co-solvent (50%/50% v/v), 1 h, FA-to-lignin mass ratio of 0.7)

As displayed in Figure 3-2, there was a negligible change in DL yield (approx. 90 wt.%) while increasing temperature up to 300 °C. The yield of SR did decrease from 4.7 wt.% to 0.1 wt.% with increasing temperature from 200 to 300 °C, which may likely be due to a capping effect of formic acid, preventing the degraded lignin intermediates from reacting further to form char ([Chakar and Ragauskas, 2004](#); [Okuda, 2004](#)). Interestingly, increasing the reaction temperature from 300 to 330 °C resulted in a drastic increase in SR yield (from ~0 wt.% to 38 wt.%), accompanied by a marked decrease in DL yield (from ~90 wt.% to ~34 wt.%). This drastic increase in SR yield and drop of DL yield probably resulted from condensation or repolymerization of the degraded lignin intermediates to form large acetone-insoluble molecules, as was observed in some previous studies ([Yuan et al., 2010](#); [Gosselink et al., 2012](#)). These results suggest that lignin degradation reactions are dominant at temperatures <300 °C) while repolymerization reactions become predominant at >300 °C. Thus, it appears that 300 °C is the optimal temperature for lignin degradation in ethanol-water co-solvent medium in the presence of formic acid, as similarly concluded a previous study by our group on

hydrothermal liquefaction of sawdust in water-ethanol co-solvent (50/50 v/v) (Cheng et al., 2010).

In contrast to the trends DL and SR yields, the  $M_n$  and  $M_w$  of the DL products decreased continuously from 900 and 6120 g/mol to 150 and 520 g/mol, respectively, as the temperature was increased from 200 to 330 °C. This suggests that the lignin reductive depolymerization via ether bond hydrolysis reaction can be promoted at higher temperatures to overcome the activation energy barrier (Gasson et al., 2012). At 330 °C, the DL product was a viscous liquid with a very low molecular weight ( $M_w \sim 600$  g/mol) at a very low yield ( $\sim 34$  wt.%) , was a viscous liquid.

### 3.3.5 Effects of substrate concentration

Feedstock concentration is another important parameter for biomass hydrothermal liquefaction as higher feedstock concentration reduces the required amount of organic solvent in the reactor and hence the costs for solvent recovery, improving the economics of the process (Pye, 1990). In a review on process condition for optimum bio-oil yield in a hydrothermal liquefaction by Akhtar et al.(2011), higher substrate concentration (or a higher biomass-to-solvent mass ratio) produced more solid residue. In this work, In a typical run, 5.0 g KL, 3 mL amount of formic acid (FA) and 30 mL water/ethanol (1:1 v/v) were loaded into the reactor, corresponding to a lignin-to-solvent mass ratio of 0.19. To examine the effect of substrate concentration on the product yields and properties, varying volumes of water/ethanol (1:1 v/v) solvent were added while keeping the KL addition amount constant (i.e., 5 g). Other reaction conditions were fixed at 300 °C, 1 h, FA-to-lignin mass ratio of 0.7. The results are summarized in Table 3-3. As a general trend observed from Table 3-3, the yield of DLs remain almost constant (85-90 wt.%) irrespective of the lignin-to-solvent mass ratio. Similar results were reported by Mahmood et al. (2013) in hydrolytic depolymerization of KL with NaOH catalyst. In contrast, increasing the lignin-to-solvent mass ratio from 0.09 to 0.56 generally resulted in a slight increase in SR yield and a higher  $M_w$  for the DL, in particular when the lignin-to-solvent mass ratio was increased from 0.41 to 0.56. As seen in Table 3-3 the  $M_w$  of the DLs slightly increases from 1270 g/mol to 1450 g/mol while increasing the lignin-to-

solvent mass ratio from 0.09 to 0.41. However, when increasing the lignin-to-solvent mass ratio from 0.41 to 0.56, the  $M_w$  remarkably increased from 1450 g/mol to 1930 g/mol. Thus, taking into account of both  $M_w$  of the DL products and process economics, the optimal lignin-to-solvent mass ratio is around 0.41.

**Table 3- 3** Effects of lignin-to-solvent ratio (w/w) on yields of DL and SR (other reaction conditions: 300 °C, 1 h, water-ethanol co-solvent (50:50 v/v), FA-to-lignin mass ratio of 0.7)

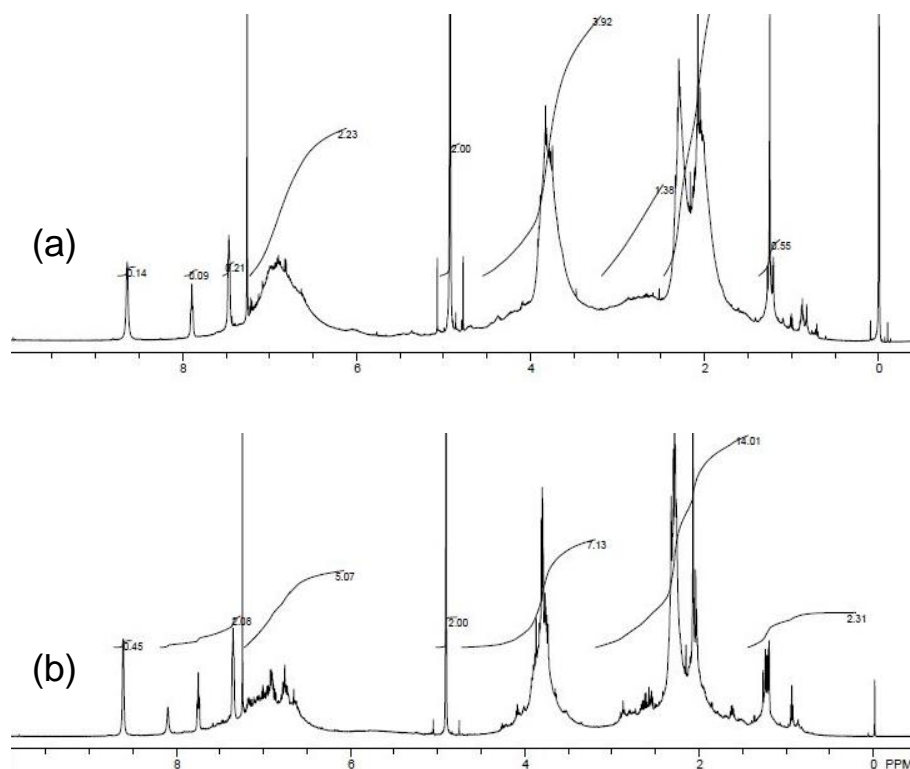
lignin-to-solvent ratio (w/w)	DL	SR	$M_n$	$M_w$	PDI
0.09	88.0( $\pm$ 0.0)	0.1( $\pm$ 0.0)	440	1300	3.0
0.19	88.0( $\pm$ 2.8)	0.5 ( $\pm$ 0.2)	410	1270	3.1
0.41	85.8( $\pm$ 0.5)	1.0( $\pm$ 0.4)	490	1450	3.0
0.56	86.3( $\pm$ 1.6)	4.6( $\pm$ 0.6)	610	1930	3.2

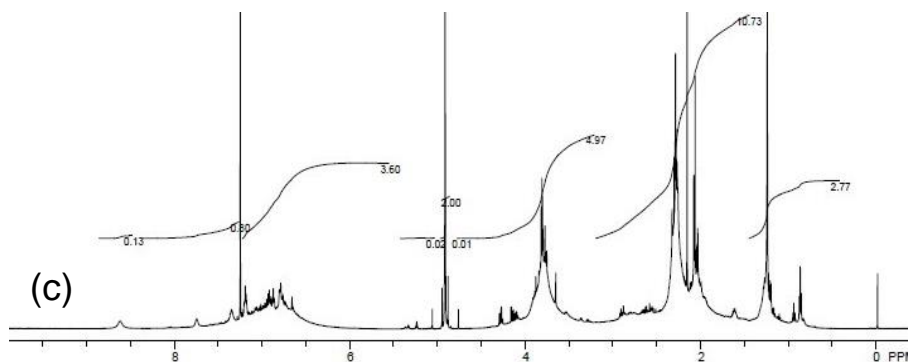
### 3.3.6 Chemical analyses of the DL products

Quantitative  $^1\text{H}$  NMR analysis was conducted to measure the hydroxyl number of DLs and the original KL using acetylated samples of KL and DLs (the acetylation was performed to improve their solubility in d-chloroform).  $^1\text{H}$  NMR spectra of the acetylated KL and DLs obtained at 300°C with 1000 psi  $\text{H}_2$  or with FA at FA-to-lignin mass ratio of 0.7 using water-ethanol co-solvent (50%/50% v/v) for 1 h are shown in Figure 3-3.  $^1\text{H}$  NMR spectra of acetylated KL /DLs showed strong signals from the internal standard (Dibromomethane) at 4.9 ppm. The signal associated with aliphatic acetates, phenolic acetates and methoxyl groups in KL or DLs are at 1.9-2.2 ppm, 2.2-2.5 ppm and 3.1-4.2 ppm, respectively (Tejado et al., 2007). Owing to the cleavage of ether linkages (e.g.,  $\alpha$ -O-4 and  $\beta$ -O-4) through hydrolytic depolymerization, the peak associated with aliphatic –OH was stronger in DL than in KL. The presence of methoxy groups ( $-\text{OCH}_3$ ) directly

connected to benzene rings can be verified by the proton signals appearing at ~3.5 ppm for both the KL and DLs.

Aliphatic and phenolic acetate protons in the acetylated samples actually represent aliphatic and phenolic hydroxyls in the non-acetylated samples. Quantification of the aliphatic and phenolic hydroxyls was made by peak integration. The contents of aliphatic and phenolic hydroxyls in the lignin are presented by hydroxyl numbers as described in [Mahmood et al., \(2013\)](#). The results are given in Table 3-4.





**Figure 3- 3**  $^1\text{H}$  NMR spectra of the acetylated KL (a) and DLs obtained at  $300^\circ\text{C}$  with 1000 psi  $\text{H}_2$  (b) or with FA at FA-to-lignin mass ratio of 0.7 (c) using water-ethanol co-solvent (50%/50% v/v) for 1 h

**Table 3- 4** Quantitative  $^1\text{H}$  NMR analysis results for acetylated KL and DLs obtained from the experiments under the following conditions:  $300^\circ\text{C}$  with 1000 psi  $\text{H}_2$  or with FA at FA-to-lignin mass ratio of 0.7, using water-ethanol co-solvent (50%/50% v/v) for 1 h.

Acetylated sample	Hydrogen source	Aliphatic hydroxyl number (mg KOH/g)	Total hydroxyl number (mg KOH/g)
KL		128	275
DL	1000 psi $\text{H}_2$	237	384
DL	3 mL FA	256	466

As presented in Table 3-4, both DLs produced have a total hydroxyl number of 384-466 mg KOH/g and an aliphatic hydroxyl number of 237-256 mg KOH/g, greater than that of the original KL (275 mg KOH/g total OH number and 128 mg KOH/g aliphatic OH number). It is also an interesting observation that the DL obtained with formic acid has a higher aliphatic-OH number in comparison with that with  $\text{H}_2$  gas. This could be attributed to the higher reactivity of the hydrogen atom *in-situ* generated from FA than  $\text{H}_2$  gas, leading to more aliphatic ether bond cleavage by the *in-situ* H from FA ([Gosselink,](#)

et al., 2012). Another interesting finding is that the hydroxyl numbers of DLs through reductive depolymerization in this work are lower than those in the DLs from alkaline hydrolytic depolymerization of the same KL (total OH number 300–800 mg KOH/g) (Mahmood et al., 2013; Jin et al., 2011). The above quantitative  $^1\text{H}$  NMR analysis results imply that the obtained DLs can be used as a bio-replacement for petroleum-based polyols for the production of PU foam or as a phenol substitute in PF resins (Bari, 2012; El Mansouri et al., 2006).

Elemental analysis was carried out to measure the CHNSO elemental composition of the DL samples and to examine the carbon recovery of the hydrolytic depolymerization experiments with FA. As typical results, Table 3-5 provides the elemental analyses of original KL and DLs from the KL depolymerization in ethanol-water co-solvent (50/50, v/v) at 300 °C for 1 h with FA at various FA-to-lignin ratios. The depolymerization of kraft lignin with or without formic acid can significantly reduce the sulfur content (from 1.52 wt.% in KL to 0.6-0.9 wt.% in DLs) and slightly decrease the oxygen content (from 25.67 wt.% in KL to ~23 wt.% in DLs) – typical of the hydro-de-sulfurization (HDS) and hydro-de-oxygenation (HDO) effects, leading to slightly decreased O/C atomic ratio and slightly increased H/C atomic ratio for the DL products. An increase in FA-to-lignin mass ratio does not appear to have an effect on the elemental composition of the DLs.

**Table 3- 5** Elemental composition of the KL and the DLs from the KL depolymerization in ethanol-water co-solvent (50/50, v/v) at 300°C for 1 h with FA at various FA-to-lignin ratios

FA-to-lignin ratio (w/w)	DL yield (wt.%)	Elemental composition of DL (wt.%)						
		N	C	H	S	O	O/C	H/C (-)



Original KL	-	0.03	62.23	5.59	1.52	25.7	0.31	1.08
0	71.5( $\pm 0.4$ )	0.11	68.8	5.87	0.86	23.0	0.25	1.03
0.2	84.2( $\pm 0.4$ )	0.19	69.5	6.24	0.88	23.2	0.25	1.08
0.7	88.0( $\pm 2.8$ )	0.04	70.6	6.39	0.76	22.8	0.24	1.09
1.5	87.6( $\pm 0.1$ )	0.13	69.9	6.21	0.70	23.1	0.25	1.06
2.4	86.7( $\pm 0.2$ )	0.09	69.8	6.19	0.62	23.6	0.25	1.06

Since FA decomposes at elevated temperatures, producing H<sub>2</sub> and CO<sub>2</sub>, as evidenced later in Figures 3-4 and 3-5, the carbon in the gas phase comes from both FA and the lignin de-gradation. In this work, the total carbon recovery was calculated only based on the carbon distributions in SR and DL products. It should be noted that SR was not sufficient for elemental analysis in some experiments due to their very low yields. Table 3-6 presents carbon distribution in the SR and DL products and total carbon recovery from typical experimental runs under different conditions (FA-to-lignin mass ratio of 0.7, 1h). The results in the Table 3-6 clearly show that for most experiments, e.g., within ethanol-water medium with 0-50 vol.% ethanol at 300 °C for 1 h, the total carbon recovery was mostly in a range of 90-103 wt.%, which is satisfactory considering the unavoidable errors in the experiments, product recovery and analysis. For some runs in 50 vol.% ethanol-water medium at a higher temperature (i.e., 330 °C) or in ethanol-water medium with 75 vol.% ethanol at 300 °C, the total carbon recovery was as low as ~75 wt.%. This is reasonable and can be explained by the formation of relatively larger amounts of low-boiling point compounds from the KL (lost in rotary evaporation during DL product recovery) under such reaction conditions.

**Table 3- 6** Carbon distributions in the SR and DL products and total carbon recovery from typical experimental runs under different conditions (FA-to-lignin mass ratio of 0.7, 1h)

Ethanol vol.% in ethanol-water medium	Temp. (°C)	Carbon distribution		
		SR	DL	Water+Gas+LBP <sup>1</sup>
0	300	25.6(±0.4)	77.0(±0.0)	0.0(±0.4)
25		2.6(±0.7)	88.0(±0.7)	9.4(±0.9)
50		0.8(±0.0)	93.8(±0.0)	5.4(±0.0)
75		29.6(±0.1)	44.3(±0.1)	26.1(±0.1)
50	330	36.0(±0.1)	39.9(±0.1)	24.1(±0.1)

<sup>1</sup>Total yield of water, gaseous products and low boiling point products (LBP) lost during evaporation, calculated by difference.

As the sulfur content of DLs has been reduced significantly after the treatment, further analysis has been carried on the sulfur content of the SRs. Table 3-7 presents the sulfur distribution in the SR, DL and gas products from typical experimental runs. Most of sulfur in KL (50-80 wt.%) ended in the gaseous products after lignin depolymerization.

**Table 3- 7** Sulfur distributions in the SR, DL and Gas products from typical experimental runs under different conditions (FA-to-lignin mass ratio of 0.7, 1h)

Ethanol vol.% in ethanol-water medium	Temp. (°C)	Sulfur distribution (wt.%)		
		SR	DL	Gas <sup>1</sup>
0	300	1.40(±0.39)	18.44(±0.15)	80.16(±0.42)
25		0.73(±0.82)	29.90(±0.12)	69.37(±0.83)
50		0.00(±0.00)	43.95(±0.06)	56.05(±0.06)
75		5.02(±0.26)	19.12(±0.08)	75.87(±0.27)
50	330	3.72(±0.37)	8.15(±0.34)	88.13(±0.51)

<sup>1</sup>Sulfur in the gaseous products, calculated by difference.

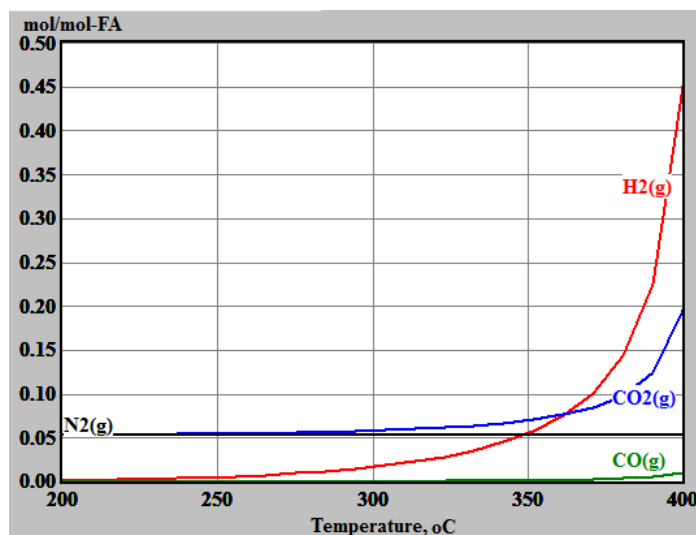
## 4. Discussion

### 3.4.1 Roles of FA in lignin depolymerization

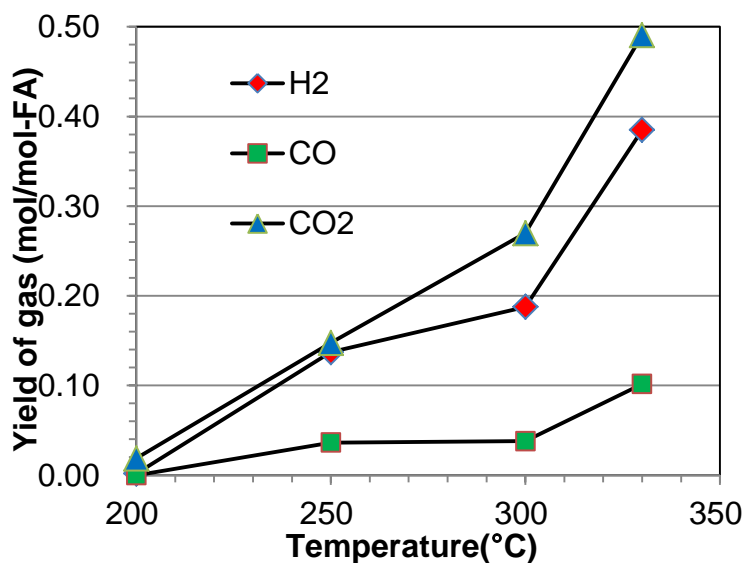
From the results displayed in Table 3-1, it is clear that the presence of FA led to decreases in both molecular weights and PDI of the DL products, accompanied by an increase in DL yield and reduction in SR. The role of formic acid in lignin depolymerization needs to be discussed. The positive effects of the presence of FA in the process is likely due to the hydrogen donation effects of formic acid and the hydrogen produced from FA decomposition, which can suppress the repolymerization reactions involving the reactive degraded products (Yu and Savage, 1998; Kleinert, et al., 2009).

Formic acid is not stable at elevated temperatures, as it can decompose to form  $H_2$  and  $CO_2$  ( $HCOOH \rightarrow H_2 + CO_2$ ). Using HSC 5.1 software, the equilibrium yields of gaseous species based on thermodynamic calculations, were calculated for the reaction system (FA-to-lignin ratio of 0.7, ethanol-water co-solvent (50/50, v/v), 1 h, 300 °C, 2 MPa initial  $N_2$  pressure), and the results are illustrated in Figure 3-4. As indicated in the figure, decomposition of formic acid, forming  $H_2$  and  $CO_2$ , starts at a temperature lower than 200 °C, and becomes significant above 300 °C. The yields of gaseous products,  $CO_2$ ,  $H_2$  and CO (in mole/mol-FA) at various temperatures in ethanol-water co-solvent (50/50, v/v) at FA-to-lignin mass ratio of 0.7 for 1 h were also measured in the experiments and presented in Figure 3-5. As shown in the Figure 3-5, the experimental measurements are in a good agreement with the predictions based on thermodynamic calculations (Figure 3-4), e.g., decomposition of formic acid, forming  $H_2$  and  $CO_2$ , starts at approx. 200 °C. Comparing these two figures, there are some differences. For example, the yield of  $H_2$  is much lower than that of  $CO_2$  up to 330°C in the experimental measurements (Figure 3-5), while according to the thermodynamic calculations  $H_2$  yield increases much faster than the  $CO_2$  yield, especially at temperature >300 °C. This difference may be explained by the fact that in the KL depolymerization experiments,  $H_2$  from FA decomposition is partially consumed to hydrogenate ether linkages the KL, which would decrease the  $H_2$  present in the gas phase. The increased formation and consumption of  $H_2$  at higher

temperatures may be a key factor in decreasing the  $M_w$  of the DL products, as evidenced by the results presented in Figure 3-4.

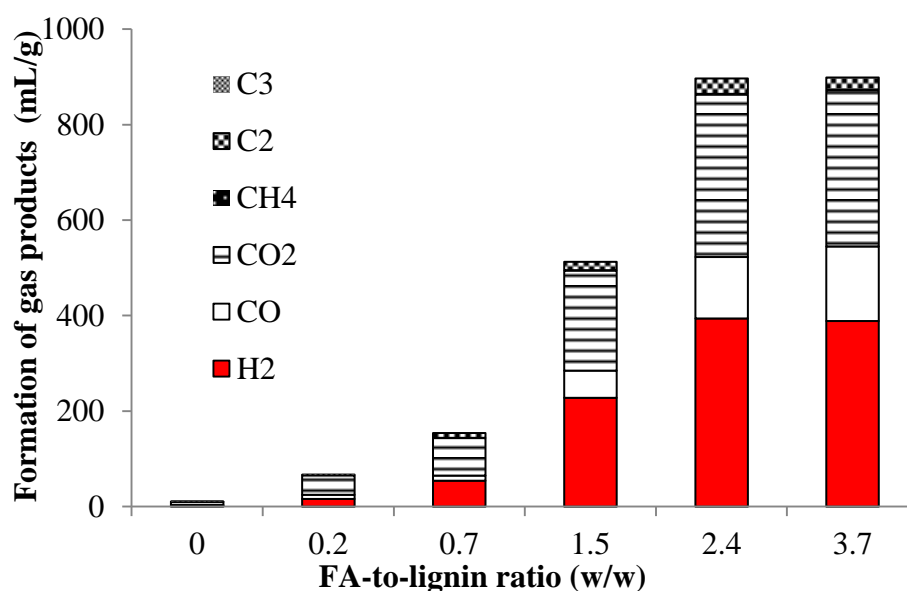


**Figure 3- 4** Equilibrium yields of gaseous species, calculated using HSC 5.1 software for the reaction system under the condition of (FA-to-lignin mass ratio of 0.7, ethanol-water co-solvent (50/50, v/v), 1 h, 300 °C, 2 MPa initial  $N_2$  pressure)



**Figure 3- 5** Yields of gas products (in mole/mol-FA) at various temperatures in ethanol-water co-solvent (50/50, v/v) at FA-to-lignin mass ratio of 0.7 for 1 h

Figure 3-6 shows the formation of gas products from the experiments with various FA-to-lignin ratios in ethanol-water co-solvent (50/50, v/v) at 300°C for 1 h. As clearly shown in the Figure 3-6, the amount of gas formation for experiments without formic acid was negligible, which implies that the gas formation from ethanol decomposition and lignin depolymerization was minimal. In contrast, large amounts of gases ( $\text{CO}_2$ ,  $\text{H}_2$  and  $\text{CO}$  in particular) were produced in all of the runs using formic acid, as shown in Figures 4 and 5 and similarly reported in the studies of [Yu and Savage \(1998\)](#) and [Kleinert et al. \(2009\)](#). From Figure 3-6, there is a very obvious trend that the formation of  $\text{H}_2/\text{CO}_2/\text{CO}$  increases with increasing FA-to-lignin mass ratio, which may explain the decrease in both molecular weights and PDI of the DL products at a higher FA-to-lignin mass ratio (Table 3-1).



**Figure 3- 6** Effect of FA-to-lignin mass ratio on the formation of gas product (ethanol-water co-solvent (50/50, v/v), 1 h, 300 °C)

### 3.4.2 Effects of hydrogen source

In this study, different hydrogen sources, namely external 1000 psi hydrogen gas (as the pressurizing gas for the 100 mL reactor) and 3 mL FA, were employed for the depolymerization of 5.0g kraft lignin in 30 mL 50/50 v/v water-ethanol co-solvent at 300

°C for 1 h. Assuming ideal gas behavior and 100% decomposition of FA (to form CO<sub>2</sub> and H<sub>2</sub>), 38.0 and 15.9 mol H<sub>2</sub>/kg lignin was available for the experiments involving 1000 psi hydrogen and 3 mL FA, respectively. The yields of DL and SR and GPC analysis results for the DL products from the KL depolymerization with different hydrogen sources, but at the same other conditions (50/50 v/v water-ethanol co-solvent at 300 °C for 1 h) were compared in this work.

The results (Table not shown), irrespective of hydrogen source, the molecular weight  $M_w$  and  $M_n$  as well as PDI were in the narrow ranges of 1230-1270 g/mol, 410-430 g/mol and 3.0-3.1, respectively. Larger differences were observed between the yields of DL and SR when using different hydrogen sources. The use of 3 mL FA (corresponding to 15.9 mol-H<sub>2</sub>/kg-lignin) produced ~88.0 wt.% DL and ~0.5 wt.% SR, compared with ~56.0 wt.% DL and ~29.1 wt.% SR with 1000 psi hydrogen gas (corresponding to 38.0 mol-H<sub>2</sub>/kg-lignin). The above results indicate the source of hydrogen (either in the form of pure H<sub>2</sub> gas or FA) has little effect on the molecular weights of the DL products, while it drastically affects the product yields. The runs using FA increased DL yield over 50 wt.% and greatly decreased SR yield (29 wt.% vs 0.5 wt.%) even though pressurizing the reactor with 1000 psi H<sub>2</sub> provided more than twice the hydrogen than the runs using FA.

Thus, FA is a more reactive hydrogen source than external hydrogen atmosphere for the reductive depolymerization of KL. The *in-situ* hydrogen produced by the decomposition of FA during the reaction may participate in the reaction while still in H atom form, hence it is more reactive (Kleinert and Barth, 2008a, b; Kleinert et al., 2009). In contrast, the external hydrogen atmosphere is present in molecular H<sub>2</sub> form that needs to dissociate into H atoms before participating in any the reactions (and is therefore less reactive).

### 3.5 Conclusions

Employing formic acid (FA) as an *in-situ* hydrogen source in ethanol/water mixture solvent media, kraft lignin (KL) was effectively depolymerized. At the optimum conditions (300 °C, 1 h, ethanol-water (50/50 v/v) and FA-to-lignin mass ratio of 0.7-2.4), KL ( $M_w$  10,000 g/mol) was depolymerized into depolymerized lignin (DL) - a low-

molecular weight product ( $M_w \approx 1270$  g/mol) at a high yield of  $\sim 90$  wt.%. The sulfur content was also significantly reduced from 3.1 wt% (in KL) to 0.6 wt.% (in DL). The FA was demonstrated to be a more reactive hydrogen source than external hydrogen for reductive depolymerization of KL.

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## Chapter 4 Reductive Depolymerization of Kraft Lignin for Bio-chemicals or Fuels in Formic Acid with Supported Metal Catalysts

### 4.1 Introduction

Lignin is an abundant renewable feedstock contained in woody and plant biomass with unique poly-aromatic structure. It is a by-product from the kraft pulping industry, generated in a large quantity of ~ 50 Mt/year worldwide. Kraft lignin in the form of “black liquor” is currently burnt in paper mills and cellulosic ethanol plants for producing heat and electricity – which is considered as a low value application of lignin. However, lignin if separated from “black liquor” using some lignin precipitation processes such as LignoBoost process (Tomani, 2010) or Lignoforce process (Kouisni et al., 2012), can be depolymerized/liquefied liquid products of a lower molecular weight for fuels, chemicals and bio-products.

Crude lignin has low reactivity due to lesser accessibility to the available reactive groups, caused by the steric hindrance effect of its highly branched molecular structure. In the light of the characteristic structure of lignin, partial destruction of the bulk structure would increase its reactivity, miscibility and compatibility with other chemicals and liberate more reactive functional groups such as phenolic ring and pendant hydroxyl groups. Bio-phenol-formaldehyde (BPF) resins synthesized using depolymerized lignin were achieved in our lab and demonstrated greater bonding strength than a neat PF resin as adhesive for plywood even at phenol substitution ratio up to 75-90 wt.% (Cheng et al., 2013). In other work, a curing agent for epoxy resin was prepared from a polycarboxylic acid containing depolymerized lignin and exhibited a comparable storage modulus to commercial hexahydrophthalic anhydride (HHPA) (Qin et al., 2013). These results suggest that partial depolymerization of lignin may present a viable approach for converting lignin into useful aromatic chemicals.

The reductive depolymerization of lignin is an attractive route for the conversion of lignin into valuable aromatic chemicals, fuel, and materials. Nevertheless, very few studies appeared until recently some homogeneous and heterogeneous catalysts were reported for depolymerization of lignin and lignin model compounds (Zakzeski et al., 2010; Pandey and Kim, 2011). The reductive depolymerization requires metal catalysts and high pressure hydrogen. Cheng et al. (2013) conducted catalytic hydrothermal liquefaction of lignin and employed Ru<sub>10%</sub>/Al<sub>2</sub>O<sub>3</sub> and Ni<sub>10%</sub>/AC as catalysts. Low molecular weight of <2,000 g/mol depolymerized lignin was obtained at a high yield >90 wt.%, and the depolymerized lignin products exhibited good performance in the synthesis of bio-PF resin. Xin et al. (2014) found that partial depolymerization of enzymolysis lignin via mild hydrogenolysis over raney nickel enhanced the solubility of the depolymerized lignin and reduced the molecular weight with increased hydroxyl numbers. Song et al. (2013) reported that the reduced nickel-based catalysts played an important role in the hydrogenolysis of the C-O-C bonds in two lignin model compounds.

However, the processes discussed above require high-pressure external hydrogen, increasing the infrastructure costs in terms of supplying of high-pressure H<sub>2</sub> gas and recycling and purification of the un-reacted hydrogen. A different way to supply hydrogen to the reactor system is to use formic acid as internal hydrogen source. Gasson et al (2012) and Forchheim et al.(2012) carried out kinetic modeling studies of lignin depolymerization in ethanol/formic acid solvent and suggested that catalytic reductive depolymerization using formic acid could be a good way to increasing the recovery of demethoxylated phenolics in the bio-oil product. So far, no research has been conducted investigating catalytic reductive depolymerization of kraft lignin using formic acid as internal hydrogen in water-ethanol mixture proved to be very effective for lignin depolymerization (as reported in Chapter 3). In this study, nickel and ruthenium, two commonly used metal catalysts for ether bonds hydrogenation were chosen for reductive depolymerization of kraft lignin. Water-ethanol mixture (50/50 v/v) was used as the reaction medium and formic acid was used as the *in-situ* hydrogen source for the kraft lignin depolymerization.

## 4.2. Materials and Experimental Methods

### 4.2.1 Materials

Kraft lignin (KL) was provided by FP innovations-Thunder Bay Bio-economy Technology Center. The  $M_w$  and  $M_n$  of KL determined by GPC-UV are  $\approx 10,000$  g/mol and  $\approx 5,000$  g/mol, respectively. The dried sample of KL contained 0.57 wt.% ash and 1.52 wt.% sulfur (on a dry-ash-free basis). In this study, ACS reagent grade solvents and chemicals, including ethanol, acetone and formic acid (>95 wt.%) were used. In the GPC analysis for the liquid products, HPLC grade solvent of tetrahydrofuran (THF) was used, which contained 0.03 wt.% stabilizer of 2, 6-di-*t*-butyl-4-methyl-phenol. The catalysts used in this research were Ni<sub>10%</sub>/Al<sub>2</sub>O<sub>3</sub>, Ni<sub>10%</sub>/Zeolite, Ru<sub>10%</sub>/Al<sub>2</sub>O<sub>3</sub>, Ru<sub>10%</sub>/C and FHUDS-2.

### 4.2.2 Catalyst preparation

Two commercial catalysts were employed in this work for lignin depolymerization, namely, Ru<sub>5%</sub>/C obtained from Sigma Aldrich and FHUDS-2 - the W-Mo-Ni type catalyst developed by Fushan Research Institute of Petroleum & Petrochemicals (FRIPP). The detailed composition of the FHUDS-2 was not disclosed due to the confidentiality. Ru<sub>5%</sub>/C catalyst was used as received without further treatment (such as calcination or reduction).

The other catalysts were prepared in-house by incipient wetness impregnation using aqueous metal salt solutions of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, and H<sub>4</sub>N<sub>4</sub>O<sub>10</sub>Ru. The Al<sub>2</sub>O<sub>3</sub> used in our study was  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (gamma-alumina nanopowder) and zeolite was x-zeolite supplied by Sigma-Aldrich. The nickel-based catalysts, Ni<sub>10%</sub>/Al<sub>2</sub>O<sub>3</sub>, Ni<sub>10%</sub>/Zeolite and FHUDS-2, were calcined in N<sub>2</sub> at 550 °C for 1 h followed by 3 h reduction in hydrogen at the same temperature. The same calcinations conditions were adopted for the Ru<sub>10%</sub>/Al<sub>2</sub>O<sub>3</sub> but

without H<sub>2</sub> reduction. All the catalysts were then crushed and sieved to particle size less than 300 µm for the experimental use in this study. Textural properties of the catalysts were measured by nitrogen isothermal adsorption at 77 K on a Quantachrome Autosorb-1 instrument. Prior to the measurements, samples were de-gassed under N<sub>2</sub> purge at 523 K for 6 h. The BET surfaces and total pore volumes of fresh catalysts used in our study are showed in Table 4-1.

**Table 4- 1** Textural properties of the fresh catalysts used in this study.

Catalyst and support	BET surface area (m <sup>2</sup> /g)	Total pore volume (cc/g)	Average pore size (nm)
Al <sub>2</sub> O <sub>3</sub>	154	0.42	11
FHUDS-2	230	0.28	5
Ru <sub>5%</sub> /C	961	0.82	3
Ru <sub>10%</sub> / Al <sub>2</sub> O <sub>3</sub>	165	0.44	11
Ni <sub>10%</sub> /Al <sub>2</sub> O <sub>3</sub>	133	0.36	11
Ni <sub>10%</sub> /Zeolite	9	0.03	16

### 4.2.3 Depolymerization of lignin

The KL depolymerization was performed in a 100 mL Parr reactor with maximum working pressure of 34 MPa at 350 °C. In a typical run, 5.0 g KL, 0.5 g catalyst or 10 wt.% of the lignin (the catalyst loading amount was reduced to 0.25 g for Ru<sub>5%</sub>/C and Ru<sub>10%</sub>/Al<sub>2</sub>O<sub>3</sub> as Ru-based catalysts are very expensive), 3 mL of formic acid (FA) and 30 mL water/ethanol mixture (1:1 v/v) were loaded into the reactor. The reactor was sealed, evacuated and purged three times with N<sub>2</sub> followed by pressurizing the reactor to 2 MPa

with N<sub>2</sub>. The reactor was heated to the specified temperature (200-300 °C) for a specified time (1-3 h) under stirring at 290 rpm. After the predetermined reaction time had elapsed, the reactor was quenched in an ice-water bath to stop the reaction. The resulting gaseous products were collected in a gas bag with an injection of 500 mL of air as an internal standard and analyzed for gas composition (H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>-C<sub>3</sub>) with a Micro-GC. The remaining reaction products were rinsed from the reactor with acetone followed by vacuum filtration through a pre-weighed filter paper. The acetone-soluble fraction was isolated by rotary evaporation under reduced pressure at 40-60 °C to remove the organic solvents and residual water. The resulting liquid phase after evaporation was designated as depolymerized lignin (DL), and was vacuum dried at room temperature overnight before weighing. The residue after filtration was oven dried at 105 °C for 24 h to obtain the weight of the solid residue (SR). The yields of DL and SR are calculated as follows:

$$DL \text{ yield (wt.\%)} = \frac{W_{DL}}{W_{KL}} \times 100 \text{ wt\%} \quad (1)$$

$$SR \text{ yield (wt.\%)} = \frac{W_{SR}}{W_{KL}} \times 100 \text{ wt\%} \quad (2)$$

Where  $W_{DL}$  is the weight of the acetone-soluble DL,  $W_{KL}$  the weight of the dried KL and  $W_{SR}$  the weight of the obtained SR.

Different catalysts, temperatures, and reaction times were investigated to study the effects of these reaction parameters on the catalytic reductive depolymerization of KL. At least 2-3 runs were performed to ensure the reproducibility of the products yields (with relative errors in DL and SR yields within 10 wt.% between the replicate runs). The results reported in this work are mostly the average of values from the replicate runs.



#### 4.2.4 Characterization of lignin products

**Characterization of the lignin-derived products.** The composition of the gas products was analyzed by Inficon 3000 Micro-GC with TCD detectors calibrated with Prexair standard gas with H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub> gases. The DL products were subject to more comprehensive analyses including molecular weights and distribution, elemental analysis and proton nuclear magnetic resonance (<sup>1</sup>H-NMR). Molecular weights and distributions of the DL products were determined using a Waters Breeze gel permeation chromatography (GPC) instrument [1525 binary high-performance liquid chromatography (HPLC) pump; UV detector at 270 nm; Waters Styragel HR1 column at 40 °C] with THF as the eluent at a flow rate of 1 mL/min, where polystyrene standards were used for calibration. The elemental analysis was employed to investigate the C, H, O and S composition of the obtained DLs on a Thermo Fischer Flash EA 1112 series CHNS-O elemental analyzer. The results of elemental analysis were used to calculate H/C and O/C ratios of the DL products. Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra for DLs were acquired at room temperature on Varian Inova 600 NMR spectrometer equipped with a Varian 5 mm triple-resonance indirect-detection HCX probe. A total of 16-32 scans were accumulated using a 2 s recycle delay, 3.6 s acquisition time, a 45-degree tip angle (pw =4.8 us), and a spectral width from 2 ppm to 14 ppm (sw =9000.9 Hz). *d*<sub>6</sub>-DMSO and *d*-chloroform were used as the solvents for qualitative <sup>1</sup>H-NMR study. Quantitative <sup>1</sup>H-NMR analysis was conducted using acetylated samples of the KL and DLs, prepared following the procedures detailed elsewhere ([Mahmood et al., 2013](#)). The resulting acetylated KL/DLs samples were dried at 105 °C for 24 hr to remove residual water. Dibromomethane (CH<sub>2</sub>Br<sub>2</sub>) was chosen as an internal standard and the solvent selected for the quantitative analysis was *d*-chloroform. For determining hydroxyl number through <sup>1</sup>H-NMR, the samples were prepared by first weighing 15 mg of the acetylated KL or DL and 10 mg of internal standard in a vial and then the sample was transferred into a 5 mm NMR tube via a transfer pipette using *d*-chloroform (≈ 1000-1500 mg) for the subsequent <sup>1</sup>H-NMR measurements. Thermogravimetric (TG) experiments of KL and DLs were performed with a Pyris<sup>TM</sup> 1 TGA Thermal Gravimetric Analyzer from PerkinElmer Corporation,

USA, in a flow of high purity nitrogen gas at 20 mL/min. Each time, about 5-10 mg of the material was put in a platinum crucible and heated from 100 to 600 °C at a heating rate of 30 °C/min. The differential thermal analysis (DTG) was also employed to understand the thermal stability of the DL samples.

The detail distribution of the degraded lignin will not be determined as the similar results were reported in [Cheng et al.\(2012\)](#). Moreover, due to the complexity of degraded products, not all of them can be detected by Gas Chromatography- Mass Spectrometry (GC-MS) as some compounds have higher boiling point and cannot be vaporized or may decomposed into other compounds at high temperature.

**Spent catalysts characterization.** Nitrogen adsorption/desorption isotherms were obtained at 77K using a Quantachrome Autosorb-1 instrument to measure the BET surface areas and pore structure of the sample (SBET). Prior to each measurement, the sample was de-gassed under N<sub>2</sub> purge at 523 K for 6 h. The x-ray diffraction (XRD) patterns of the passivated materials were recorded on a PANalytical X'Pert PRO XRD system, using a Cu-K $\alpha$  radiation source, operated at 45 kV and 40 mA, with a scanning rate of 0.026 °/min in a 2 $\theta$  range from 6 to 97°. Thermogravimetric experiments of spent catalyst were performed in a PerkinElmer's Pyris<sup>TM</sup> 1 TGA Thermal Gravimetric Analyzer in air flow at 20 mL/min. Each time, about 5-10 mg of material were put in a platinum crucible and heated from 100 to 800 °C at a heating rate of 20 °C/min.

## 4.3. Results and Discussion

### 4.3.1 Effects of catalysts and temperature on products yields and Mw of the DLs

Table 4-2 presents the yields of DL and SR products and GPC results (number-average molecular weight  $M_n$ , weight-average molecular weight  $M_w$  and poly-dispersity index  $PDI = M_w/M_n$ ) from reductive depolymerization of KL in water-ethanol mixture (50%/50% v/v) with different catalysts at various temperatures in the range of 200-300 °C for 1 h at a FA-to-lignin mass ratio of 0.7.

In this study, the catalysts may be divided into three groups based on the metal, namely, W-Mo-Ni catalyst, Ru-based catalysts, Ni-based catalysts. Compared with the test without catalyst, the effects of all types of catalysts on the DL yield were not significant at all temperatures. All tests at all temperature, with or without a catalyst (irrespective of type of the catalysts), produced 85-95 wt.% yields of DL. This result implies that the DL yield from the KL reductive depolymerization in water-ethanol mixture (50%/50% v/v) with formic acid is determined mainly by the presence of the highly effective water-ethanol mixture with formic acid (as evidenced in Chapter 3), and less on the presence of a catalyst. However, the catalysts did significantly affect the yield of solid residue (SR) and the molecular weights and distribution of the resulted DLs. Generally, the presence of any catalyst promoted the formation of SR. For instance, the SR yield at 200 °C was 4.7(±1.7) wt.% without catalyst, while it was 7.7(±3.0) wt.% with FHUDES-2, 14.8(±2.7) wt.% with Ru<sub>5%</sub>/C, 2.8(±1.8) wt.% with Ru<sub>10%</sub>/Al<sub>2</sub>O<sub>3</sub>, 13.7(±2.1) wt.% with Ni<sub>10%</sub>/Al<sub>2</sub>O<sub>3</sub> and 9.3(±2.3) wt.% with Ni<sub>10%</sub>/Zeolite. Generally, SR is high molecular weight materials produced by condensation and repolymerization of the liquid and intermediate products from lignin degradation. The presence of a catalyst, in particular a catalyst with acidic support, would promote the repolymerization of the liquid and intermediate products into higher molecular weight materials, i.e., SR.

At 200 °C all the catalysts, except W-Mo-Ni FHUDES-2 catalyst, exhibited remarkable catalytic effect for depolymerization of KL, reducing the molecular weight  $M_w$  of KL from 10,000 g/mol to 3640-4650 g/mol for the DLs, compared with  $M_w$  of 6120 g/mol for the DL obtained without catalyst. Three catalysts, Ni<sub>10%</sub>/Zeolite, Ni<sub>10%</sub>/Al<sub>2</sub>O<sub>3</sub> and Ru<sub>5%</sub>/C, have similar activities in KL depolymerization at 200 °C, producing DL at similar yield and with similar molecular weights of 3150 g/mol, 3360 g/mol and 3640 g/mol, respectively. This result suggests that the expensive Ru-based catalyst may be replaced by the Ni-based catalysts for lignin reductive depolymerization. The reduced Ni metal catalysts supported on Al<sub>2</sub>O<sub>3</sub> or activated carbon were reported to be effective in depolymerization an organosolv lignin by hydrogen gas ([Cheng et al., 2013](#)). The reduced Ni-based catalysts also demonstrated to be more active than a Ru-based catalyst for cleavage in ether bond using lignin model compound and hydrogen atmosphere ([Song et al., 2013](#)).

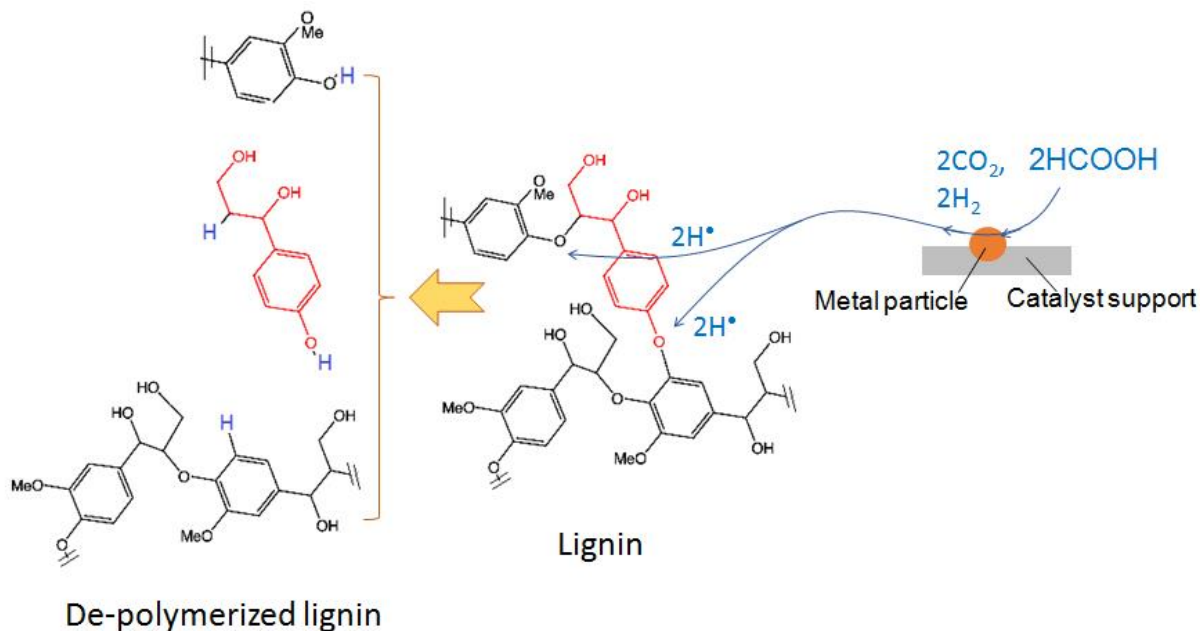
The main difference between the present lignin depolymerization reaction system from those reported in the literature is that in-situ hydrogen source via formic was used in this work, while hydrogen gas was used. Possible reaction mechanism of reductive depolymerization of lignin over a supported metal catalyst with formic acid as the in-situ hydrogen source is proposed and illustrated in Figure 4-1. The formic acid comes into contact with the metal particle to decompose into H<sub>2</sub> and dissociate into H• radicals. The H• radicals would then move into the lignin structure and cleave lignin's ether linkage by hydrogenolysis to de-polymerize macromolecules into oligomers of reduced molecular weights and remove some oxygen and double bonds by hydrogenation.

**Table 4- 2** Yields of DL, SR and molecular weight and distribution of DLs in KL depolymerization with various catalysts at different temperatures

Catalyst	Temp. (°C)	Yield (wt%) <sup>1</sup>			GPC		Reactor Pressure (MPa)
		SR	DL	$M_n$	$M_w$	PDI	

				(g/mol)	(g/mol)	(M <sub>w</sub> /M <sub>n</sub> )	
Original KL	-	-	-	~5,000	~10,000	~2.0	-
None	200	4.7(±1.7)	88.9(±3.5)	900	6120	6.8	3.4-4.1
FHUDS-2		7.7(±3.0)	91.8(±3.0)	900	6180	6.8	3.8-4.1
Ru <sub>5%</sub> /C		14.8(±2.7)	82.5(±2.5)	930	3640	3.9	3.8-5.5
Ru <sub>10%</sub> /Al <sub>2</sub> O <sub>3</sub>		2.8(±1.8)	96.1(±1.6)	940	4280	4.5	4.1-5.2
Ni <sub>10%</sub> /Al <sub>2</sub> O <sub>3</sub>		13.7(±2.1)	85.1(±0.9)	780	3360	4.3	3.4-4.5
Ni <sub>10%</sub> /Zeolite		9.3(±2.3)	93.5(±4.1)	700	3150	4.3	4.1-5.2
None	250	0.1(±0.0)	92.7(±2.1)	850	3390	4	5.9-7.2
FHUDS-2		5.3(±1.4)	85.6(±4.2)	810	3450	4.2	5.9-8.6
Ru <sub>5%</sub> /C		6.7(±0.3)	83.9(±3.0)	850	3340	3.9	6.2-9.3
Ni <sub>10%</sub> /Al <sub>2</sub> O <sub>3</sub>		11.7(±0.3)	86.7(±0.4)	760	2840	3.8	5.9-6.9
Ni <sub>10%</sub> /Zeolite		5.7(±0.2)	93.5(±3.3)	710	2540	3.6	5.9-6.9
None	300	0.6(±0.3)	88.0(±2.1)	410	1270	3.1	12
FHUDS-2		2.3(±0.1)	86.0(±0.0)	390	1080	2.7	12
Ru <sub>5%</sub> /C		2.2(±1.5)	85.7(±2.8)	550	1060	2	12
Ni <sub>10%</sub> /Al <sub>2</sub> O <sub>3</sub>		3.1(±1.6)	84.5(±4.5)	470	1270	2.7	12
Ni <sub>10%</sub> /Zeolite		0.2(±0.0)	89.4(±3.5)	420	900	2.1	12

<sup>1</sup> Other reaction conditions: ethanol-water mixture (50/50, v/v), 1 h and FA-to lignin mass ratio of 0.7.



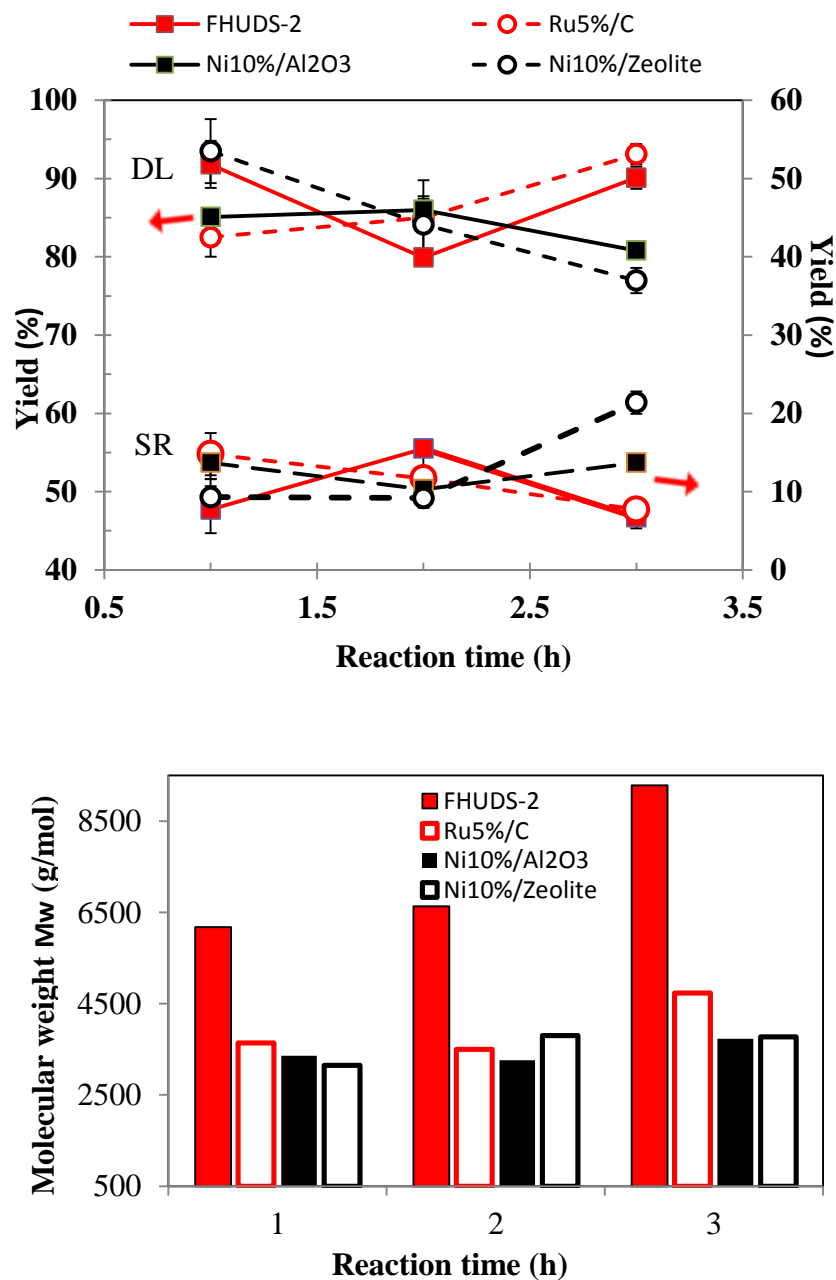
**Figure 4- 1** Possible reaction mechanism of reductive depolymerization of lignin over a supported metal catalyst with formic acid as the in-situ hydrogen source

Four catalysts: FHUDS-2, Ru<sub>5</sub>%/C, Ni<sub>10</sub>%/Al<sub>2</sub>O<sub>3</sub> and Ni<sub>10</sub>%/Zeolite were compared for their activities in lignin depolymerization at different temperatures ranging from 200 to 300 °C, while keeping the rest of reaction conditions the same, i.e., 1 h reaction, a FA-to-lignin mass ratio of 0.7 and a water-ethanol mixture (50/50, v/v). The yields of DL and SR and the molecular weights of the DL products are also displayed in Table 4-2. As presented in Table 4-2, at 300 °C, reaction without catalyst produced 0.6 wt.% yields of solid residue and 88.9 wt.% yield of DL with M<sub>w</sub> of 1270 g/mol. Comparing the treatment without catalyst at this high temperature, as mentioned previously catalyst has negligible effects on both the product yields and molecular weight of the DLs. This might be owing to the fact that the lignin depolymerization at a high temperature may be mainly controlled by thermodynamics or might be dominated by the effects of formic acid. However, when increasing temperature from 200 to 300 °C, the yield of solid residue in all tests with or without catalyst remarkably reduced, and this can be explained by that depolymerization of lignin is kinetically and thermodynamically favored at a higher temperature. The reduced SR yields at a higher temperature might also result from less

condensation of the reaction intermediates due to the un-favored entropy at a high temperature. In general, Ni<sub>10%</sub>/Zeolite performed the best in reduction of molecular weight of lignin by reductive depolymerization with formic acid at all temperatures tested. On the other hand, by increasing temperature from 200 to 300 °C, the  $M_w$  of DLs in all tests with or without catalyst significantly decreased. In terms of  $M_w$  of the DL products, Ni<sub>10%</sub>/Zeolite has the best performance at 300 °C, producing 89.4(±3.5) wt.% yield of DL of 900 g/mol  $M_w$ .

### 4.3.2 Effects of reaction time on products yields and $M_w$ of the DLs

Figure 4-2 shows the effects of reaction time on DL and SR yields in reductive depolymerization of KL at 200 °C in water-ethanol mixture (50/50 v/v) at an FA-to-lignin mass ratio of 0.7. From the Figure 4-2, the variations in both DL and SR yields with reaction time are insignificant considering the experimental errors. However, the molecular weights of DLs obtained with all catalysts tested, in particular the FHUDES-2, tend to increase while prolonging the reaction time. With other three catalysts: Ru<sub>5%</sub>/C, Ni<sub>10%</sub>/Al<sub>2</sub>O<sub>3</sub> and Ni<sub>10%</sub>/Zeolite, the effects of time on  $M_w$  of DLs are not significant. Thus, it may be concluded that reaction time is not a dominant factor in lignin depolymerization, as was also observed in a previous study by our group ([Cheng et al., 2012](#)). From Figure 4-2, the reaction time at 1 h or even shorter than 1h could be sufficient time for catalytic reductive depolymerization of kraft lignin in water-ethanol mixture with formic acid as an internal hydrogen source.



**Figure 4- 2** Effect of reaction time on the DL and SR yields and weight-average  $M_w$  of DLs in KL depolymerization at 200 °C in water-ethanol mixture (50:50 v/v) at an FA-to-lignin mass ratio of 0.7



### 4.3.3 Analyses of the DLs

#### 4.3.3.1 Elemental analysis

Elemental analysis was employed to determine the CHNSO composition of the DLs. Table 4-3 provides the elemental compositions of the obtained DL products from the lignin depolymerization process in ethanol-water mixture (50/50, v/v) at 200 and 300 °C for 1 h with and without catalyst. A general observation from the elemental analysis results show that the presence of industrial catalyst FHUDS-2 and Ni<sub>10%</sub>/Zeolite in the KL depolymerization process could significantly reduce the sulfur content in particular at a higher temperature. For instance, the sulfur content was reduced from 1.52 wt% in KL to 0.47 wt.% in the DL with Ni<sub>10%</sub>/Zeolite and 0.00 wt.% with the FHUDS-2 catalyst at 300 °C. In addition to the drastic reduction of sulfur, all catalysts appear to be effective for reducing the oxygen content in the DLs - typical of the hydro-de-sulfurization (HDS) and hydro-de-oxygenation (HDO) effects, leading to slightly decreased O/C ratio and increased H/C ratio for the DL products. The superb performance of FHUDS-2 in removing sulfur from kraft lignin by formic acid was not reported previously, but it was actually expected as FHUDS-2 has been used as an active HDS catalyst for petroleum upgrading (Yao and Yang, 2011). In contrast, the effect of Ru<sub>5%</sub>/C on sulfur content is negligible. Another trend can be observed from the elemental analysis results presented in Table 4-3 is that the O/C ratios of DLs decrease and the H/C ratios increase with increasing the reaction temperature. This suggests that the temperature plays an important role in oxygen-removal and hydrogenation.

**Table 4- 3** Elemental composition of KL and DLs from reductive catalytic depolymerization in ethanol-water mixture (50/50, v/v) at 200 and 300 °C for 1h with FA-to-lignin mass ratio of 0.7

Catalyst	Temp (°C)	Elemental composition	
		(wt.%, d.a.f.) <sup>1</sup>	O/C <sup>2</sup> H/C <sup>2</sup>

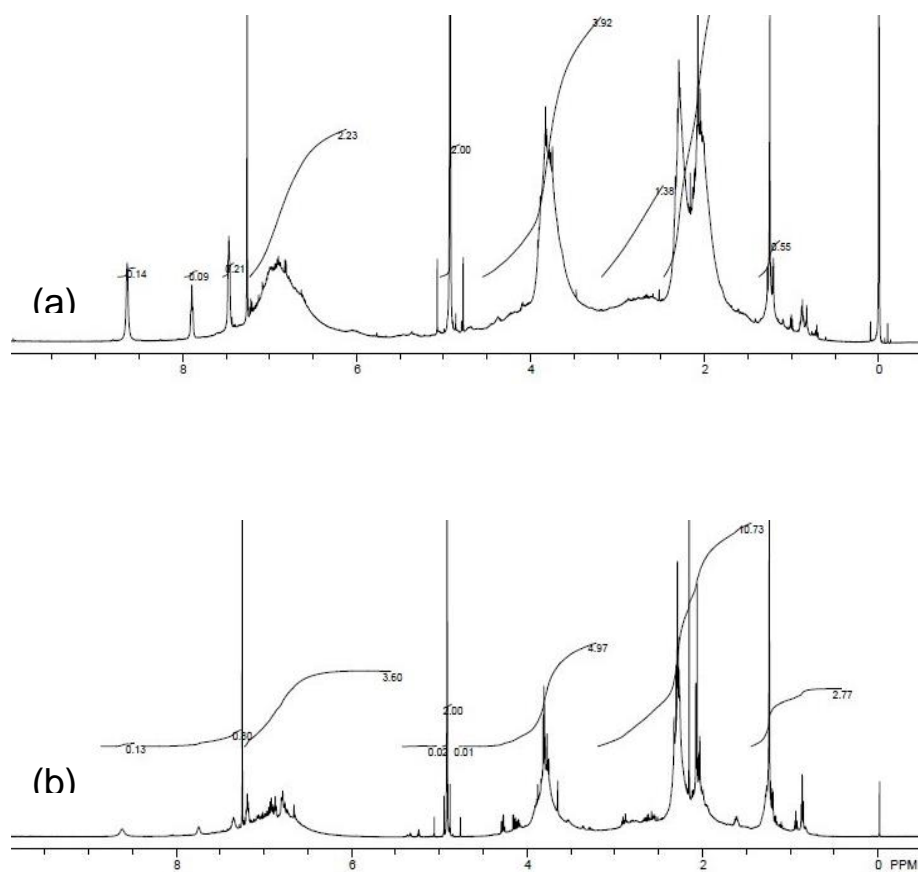
		N	C	H	S	O		
KL	-	0.03	62.23	5.59	1.52	25.67	0.31	1.08
None		0.10	66.12	4.14	1.19	25.24	0.29	0.75
Ru <sub>5%</sub> /C		0.40	64.78	5.87	1.12	24.60	0.28	1.09
FHUDS-2	200	0.10	63.97	5.86	0.89	24.34	0.29	1.1
Ni <sub>10%</sub> /Zeolite		0.10	63.54	5.39	0.73	25.16	0.30	1.02
None		0.04	70.6	6.39	0.76	22.83	0.24	1.09
Ru <sub>5%</sub> /C		0.08	72.49	6.69	0.79	22.75	0.24	1.11
FHUDS-2	300	0.08	69.42	6.31	0.00	22.47	0.24	1.09
Ni <sub>10%</sub> /Zeolite		0.10	67.14	5.98	0.47	24.47	0.27	1.07

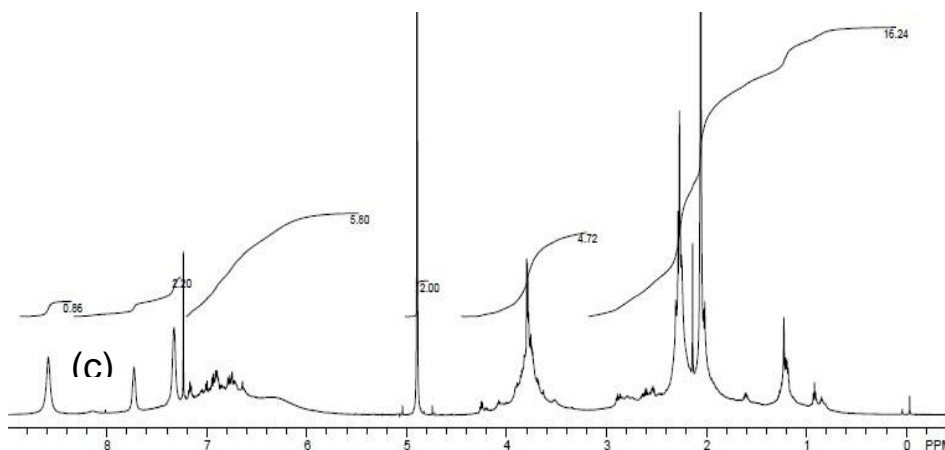
<sup>1</sup>On dry-and-ash free basis; <sup>2</sup>Atomic ratio

#### 4.3.3.2 <sup>1</sup>H NMR analysis

Quantitative <sup>1</sup>H NMR analysis was conducted to measure the hydroxyl number of DLs and the original KL using acetylated samples of KL and DLs (the acetylation was performed to improve their solubility in d-chloroform). <sup>1</sup>H NMR spectra of the acetylated KL and the 300 °C- DLs with or without catalysts at FA-to-lignin mass ratio of 0.7 using water-ethanol mixture (50%/50% v/v) for 1 h are shown in Figure 4-3. <sup>1</sup>H NMR spectra of acetylated KL/DLs showed strong signals of the internal standard (Dibromomethane) at 4.9 ppm. The signal associated with aliphatic acetates, phenolic acetates and methoxyl groups in KL or DLs are at 1.9-2.2 ppm, 2.2-2.5 ppm and 3.1-4.2 ppm, respectively

(Tejado et al., 2007). Owing to the cleavage of ether linkages (e.g.,  $\alpha$ -O-4 and  $\beta$ -O-4) through hydrogenolysis (reductive) depolymerization (Figure 4-1), the peak associated with aliphatic –OH was stronger in DL than in KL. The presence of methoxy groups (-OCH<sub>3</sub>) directly connected to benzene rings can be verified by the proton signals appearing at ~3.5 ppm for both the KL and DLs.





**Figure 4- 3**  $^1\text{H}$  NMR spectra of the acetylated KL (a) and 300°C-DLs obtained using water-ethanol mixture (50%/50% v/v) for 1 h at FA-to-lignin mass ratio of 0.7 without (b) or with  $\text{Ni}_{10\%}/\text{Zeolite}$  (c)

Aliphatic and phenolic acetate protons in the acetylated samples actually represent aliphatic and phenolic hydroxyls in the non-acetylated samples. Quantification of the aliphatic and phenolic hydroxyls was made by peak integration. The contents of aliphatic and phenolic hydroxyls in the lignin are presented by hydroxyl numbers that were defined in more details elsewhere by [Mahmood et al., \(2013\)](#). The results are given in Table 4-4.

**Table 4- 4** Quantitative  $^1\text{H}$  NMR analysis results for acetylated KL and DLs obtained from the experiments under the following conditions: 300 °C with or without catalyst at FA-to-lignin mass ratio of 0.7, using water-ethanol mixture (50%/50% v/v) for 1 h.

Acetylated sample	Hydroxyl	Hydroxyl no.(based Total –OH number (mg KOH/g)
	Aliphatic -OH	
	Number	
	(mg KOH/g)	

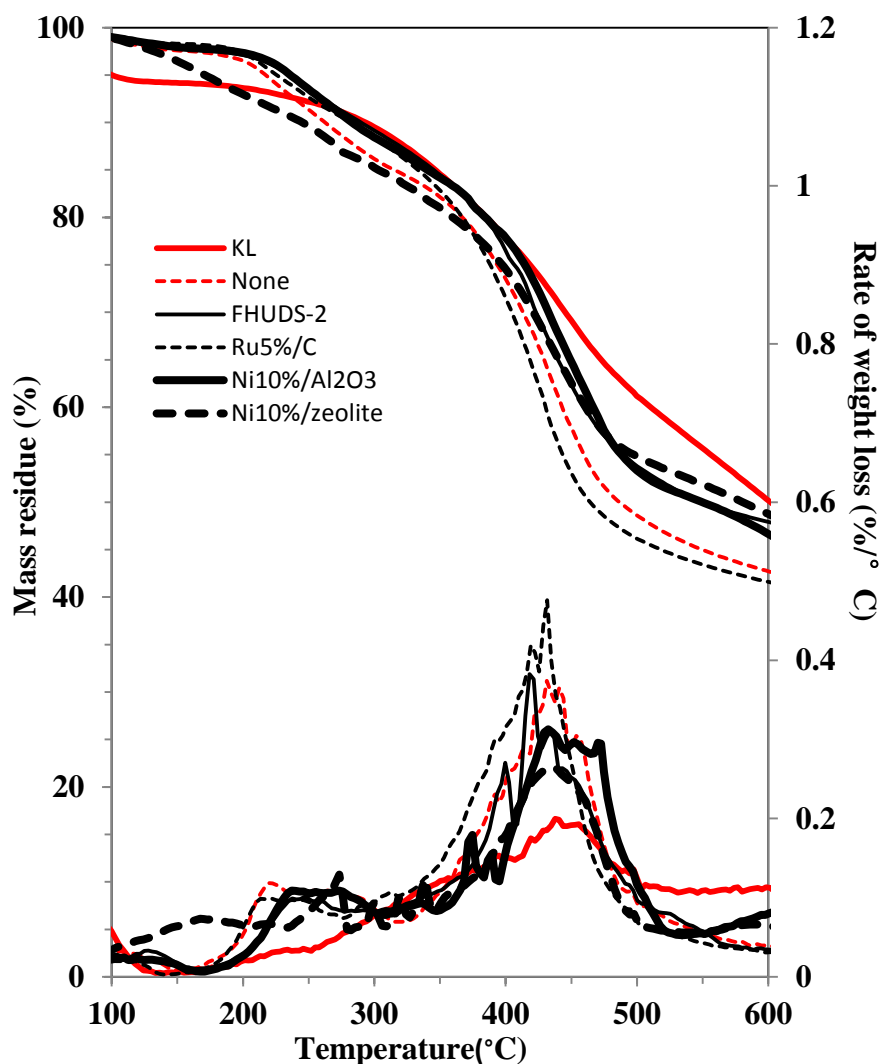
KL	128	275
None	256	466
Ni <sub>10%</sub> /Zeolite	183	392
FHUDS-2	139	347
Ru <sub>5%</sub> /C	218	374

As presented in Table 4-4, all DLs produced have a total hydroxyl number of 347-466 mg KOH/g and an aliphatic hydroxyl number of 139-326 mg KOH/g, greater than that of the original KL (275 mg KOH/g total OH number and 128 mg KOH/g aliphatic OH number). This can be explained by the cleavage of ether bond linkages (e.g.,  $\alpha$ -O-4 and  $\beta$ -O-4) that leads to formation of hydroxyl number according to the hydrolysis (reductive) depolymerization mechanism (Figure 4-1). Another interesting finding is that the hydroxyl numbers of DLs through reductive catalytic depolymerization in this work are lower than those DLs obtained without catalysts. The reduced hydroxyl number of DLs, obtained with Ni<sub>10%</sub>/Zeolite, FHUDES-2 and Ru<sub>5%</sub>/C, can be explained by the hydrogenolysis reaction and this is also evidenced by the elemental analysis with relative lower oxygen content in the DLs. The above quantitative <sup>1</sup>H NMR analysis results imply that the obtained DLs can be used as a bio-replacement for petroleum-based polyols for the production of PU foam or as a phenol substitute in PF resin synthesis ([Bari, 2012](#); [El Mansouri et al., 2006](#)).

#### 4.3.3.3 TGA/DTG analysis

TG and DTG analysis of the obtained 300 °C-DLs was conducted to investigate the thermal stability of the DL products in comparison with the original kraft lignin (KL), and the results are presented in Figure 4-4. The KL and all DLs lost weight at two peak

temperature ranges: 200-300 °C and 400-500 °C, but the two weight-loss peaks are larger for DLs than those of the KL, which means more weight loss for DLs in comparison with KL. This implies that the DL of a lower  $M_w$  is easier to decompose and lose weight upon being heated. The DL obtained with Ru<sub>5%</sub>/C exhibited the fastest decomposing rate in 400-500 °C temperature range and thus less solid residue after 600 °C. This indicates that the DL obtained with Ni<sub>10%</sub>/Zeolite exhibited the fastest decomposing rate in 100-300 °C temperature range, suggesting that it has a high content of lower boiling points compounds, as evidenced by the lowest  $M_w$  of the 300 °C-DL obtained with this catalyst.



**Figure 4- 4** TG and DTG profiles of the KL and 300°C-DLs from the KL depolymerization in ethanol-water mixture (50/50, v/v) for 1 h with FA at 0.7 mass ratio with or without catalysts

#### 4.3.4 Analysis of gaseous products

The obtained Micro-GC results with and without catalysts are showed in Table 4-5. In Table 4-5, it is obvious that Ru<sub>5%</sub>/C catalyst promotes the decomposition of formic acid even at a temperature as low as 200 °C. However, surprisingly very low amount of H<sub>2</sub>

and even zero amount of CO<sub>2</sub> were measured in the gaseous products obtained from the tests with the Ni-based catalysts (Ni<sub>10%</sub>/Al<sub>2</sub>O<sub>3</sub> and Ni<sub>10%</sub>/Zeolite) even at 300 °C. It looks like the presence of these Ni-based catalysts suppressed the decomposition of formic acid. Whereas this is not possible as formic acid is not stable at a temperature higher than 200°C regardless of the presence of a catalyst according to the thermodynamic calculation (the results were presented in the previous chapter, Chapter 3). Thus, the formic acid must decompose to give CO<sub>2</sub> and H<sub>2</sub> in the presence of the Ni-based catalysts. The low detection amount for H<sub>2</sub> and almost zero amount of CO<sub>2</sub> in the gaseous products from the tests in the presence of Ni<sub>10%</sub>/Al<sub>2</sub>O<sub>3</sub> and Ni<sub>10%</sub>/Zeolite might be due to the strong adsorption of hydrogen and carbon dioxide by Al<sub>2</sub>O<sub>3</sub> and zeolite (Ward and Habgood, 1965; Kramer and Andre, 1979; Du and Wu, 2006). Moreover, there is more hydrogen left in the gaseous product from the test with Ni<sub>10%</sub>/Al<sub>2</sub>O<sub>3</sub> in comparison that with Ni<sub>10%</sub>/Zeolite. This may be explained by the fact that zeolites have better performance than alumina in hydrogen uptake (Nijkamp et al, 2001). The adsorption effect of the Ru<sub>5%</sub>/C is much less compared with the Ni-based catalysts, because on one hand, C is not as effective as Zeolite or Al<sub>2</sub>O<sub>3</sub> for H<sub>2</sub>/CO<sub>2</sub> adsorption. On the other hand, Ru cannot adsorb hydrogen even at room temperature (Danielson et al., 1978). The reason for the presence of CO almost in all gaseous products may be the decomposition of formic acid into hydrogen, carbon dioxide and carbon monoxide which was already discussed by the thermodynamic calculation in Chapter 3.

**Table 4- 5** Yields of gas products from the KL depolymerization at various temperatures in ethanol-water mixture (50/50, v/v) at FA-to-lignin mass ratio of 0.7 with and without catalysts.

Catalyst	Temperature	Yield
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	(°C)	(mol/mol-FA)		
		H <sub>2</sub>	CO	CO <sub>2</sub>
None	300	0.186	0.038	0.268
	250	0.136	0.036	0.146
	200	0.002	0.000	0.018
Ru <sub>5%</sub> /C	300	0.313	0.014	0.436
	250	0.238	0.000	0.265
	200	0.226	0.003	0.252
Ni <sub>10%</sub> /Al <sub>2</sub> O <sub>3</sub>	300	0.100	0.047	0.000
	250	0.066	0.005	0.000
	200	0.035	0.001	0.000
Ni <sub>10%</sub> /Zeolite	300	0.047	0.145	0.000
	250	0.046	0.028	0.000
	200	0.013	0.004	0.000

#### 4.3.5 Characterization of the spent catalysts

The textural properties of the spent catalysts of Ni<sub>10%</sub>/Al<sub>2</sub>O<sub>3</sub>, Ni<sub>10%</sub>/Zeolite and Ru<sub>5%</sub>/C were measured and compared with those of the fresh catalysts, as shown in Table 4-6. For Ni<sub>10%</sub>/Al<sub>2</sub>O<sub>3</sub>, its BET surface area, total pore volume and average pore width all decreased in the spent catalysts after the reaction, in particular at a higher reaction temperature. For example, BET surface area of Ni<sub>10%</sub>/Al<sub>2</sub>O decreased sharply from 133 m<sup>2</sup>/g (fresh catalyst) to 47 m<sup>2</sup>/g for the spent catalyst at 200 °C, 28 m<sup>2</sup>/g at 300 °C.

Meanwhile, its total pore volume was reduced from 0.36 cc/g (fresh catalyst) to 0.09 cc/g at 200 °C and 0.06 cc/g at 300 °C. The reduction in both surface area and pore volume of the catalyst after the lignin depolymerization reaction might be caused by the deposition of SR product (large molecular weight materials insoluble in acetone) inside the pores of the catalyst, which might narrow the pores, plug some micropores and hence reduce the BET surface area. The deposition of SR in the spent catalysts was evidenced by the TGA and XRD measurements whose results are presented in the following sections. With Ru<sub>5%</sub>/C catalyst, after 200 °C reaction, the BET surface area of the catalyst dropped sharply from 961 m<sup>2</sup>/g to 0.2 m<sup>2</sup>/g, accompanied by the drastic decrease in total pore volume from 0.82 cc/g to 0.001 cc/g. It can also be observed that the average pore size of Ru<sub>5%</sub>/C surprisingly increased from 3 nm to 16 nm, likely due to the plugging of the micropores and some small mesopores, which explains the dramatic decreases in surface area and total pore volume.

The Ni<sub>10%</sub>/Zeolite did not exhibit great difference in total pore volume before and after reaction at 200°C, but quite interestingly, the BET surface area increased from 9 m<sup>2</sup>/g to 29 m<sup>2</sup>/g and the average pore size increased from 1.6 nm to 3.7 nm before and after the 200°C reaction. The increase in the average pore size implies plugging of some micropores or small mesopores by the SR deposits.

**Table 4- 6** BET surface and total pore volume and average pore size of fresh and spent catalysts of Ni<sub>10%</sub>/Al<sub>2</sub>O<sub>3</sub>, Ni<sub>10%</sub>/Zeolite and Ru<sub>5%</sub>/C after the KL depolymerization experiments at different temperatures

Catalyst		Original	Spent catalysts		
			200 °C	250 °C	300 °C
Ni <sub>10%</sub> /Al <sub>2</sub> O <sub>3</sub>	BET surface area (m <sup>2</sup> /g)	133	47	73	28

	Total pore volume (cc/g)	0.360	0.090	0.140	0.060
	Average pore size (nm)	11	8	7	9
Ni <sub>10%</sub> /Zeolite	BET surface area (m <sup>2</sup> /g)	9	29	n.a.	n.a.
	Total pore volume (cc/g)	0.030	0.026	n.a.	n.a.
	Average pore size (nm)	1.6	3.7	n.a.	n.a.
Ru <sub>5%</sub> /C	BET surface area (m <sup>2</sup> /g)	961	0.2	n.a.	n.a.
	Total pore volume (cc/g)	0.820	0.001	n.a.	n.a.
	Average pore size (nm)	3	16	n.a.	n.a.

It is thus of great interest in elucidating the mechanism that caused the increased BET surface area of the Ni<sub>10%</sub>/Zeolite catalyst in the spent catalyst. Some possible reasons were proposed:

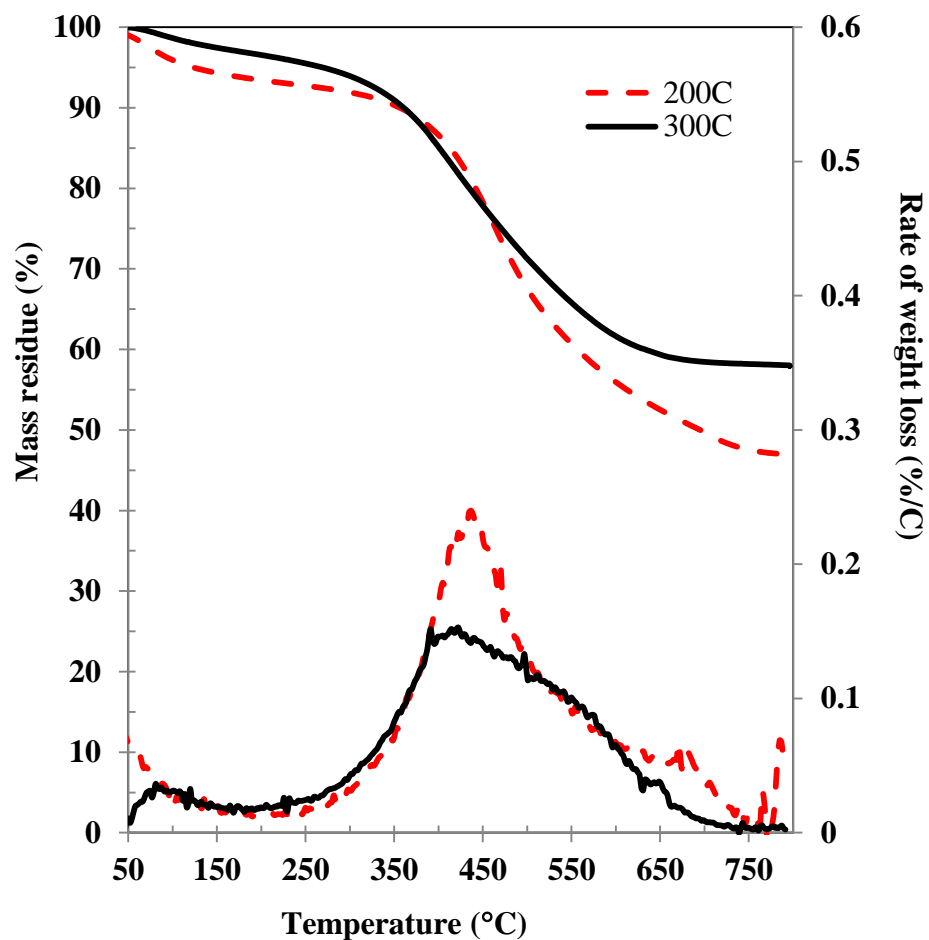
- (1) From Table 4-2, 10 wt.% SR yield was determined in the 200 °C test with Ni<sub>10%</sub>/Zeolite. Thus, formation of amorphous fine carbon (SR,) particles of a high specific surface area on the catalyst's surface could increase the overall BET surface area of the spent catalyst.
- (2) The collapsing of the crystalline structure of the Zeolite support would form amorphous structure of Al-Si oxides with a high surface area;

In order to get some insights and find some evidence for the above two possible causes, TGA and XRD analyses were carried out on the spent Ni<sub>10%</sub>/Zeolite catalyst, as shown in Figures 5 and 6, respectively.

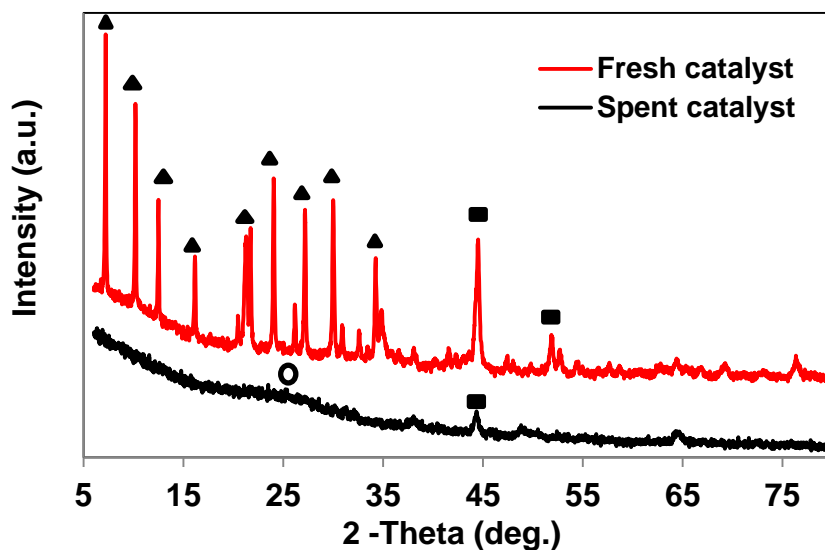
Figure 4-5 showed the TG and DTG profiles of the spent Ni<sub>10%</sub>/Zeolite catalysts from the KL depolymerization in ethanol-water mixture with formic acid at 200 and 300 °C for 1

h. When being heated in air from room temperature to 800 °C, the spent catalysts lost their weights mainly in the temperature range from 250-300 to 700-750 °C, typical of combustion loss of the carbon deposits on the catalyst. From the mass loss between the 100 and 800 °C, attributed to the carbon deposition, the carbon/coke deposition was severer in the 200 °C-spent catalyst than the 300 °C-spent Ni<sub>10%</sub>/Zeolite, which is in a good agreement with the amount of SR yields being higher at the 200 °C test (9.3 (±2.3) wt.%) than at the 300 °C test (0.2 wt.%) as presented previously in Table 4-2. Thus, the significantly deposited carbon on the 200 °C-spent Ni<sub>10%</sub>/Zeolite catalyst could contribute to the increased surface area of the catalysts if the carbon is present in amorphous fine particles.

The XRD patterns of fresh and spent Ni<sub>10%</sub>/Zeolite catalyst from the 200 °C test are showed in Figure 4-6. In the fresh Ni<sub>10%</sub>/Zeolite catalyst (after hydrogen reduction), strong diffraction lines from X-type zeolite support were detected at  $2\theta = 7.2^\circ, 10.2^\circ, 12.5^\circ, 16.1^\circ, 21.7^\circ, 24.0^\circ, 27.2^\circ, 30.0^\circ$  and  $34.4^\circ$  (El-Naggar et al., 2008), as indicated in the Figure. In addition, strong XRD diffraction peaks of reduced Ni metal (face-centered cubic crystalline structure) were also observed at  $2\theta = 44.5^\circ$  and  $51.9^\circ$  (Lai et al., 2006). From the XRD patterns of the 200 °C-spent Ni<sub>10%</sub>/Zeolite catalyst, surprisingly all the diffraction lines of X-type zeolite support disappear, which evidences the collapsing of the crystalline structure of the zeolite support during the reaction under the relatively harsh conditions used in the tests (200 °C hot-compressed water-ethanol mixture with formic acid). The deposition of carbon on the catalyst was also evidenced by the characteristic wide carbon (002) peak at  $2\theta = 24-26^\circ$ . The sharp peak at  $2\theta = 44.5^\circ$  in the spent Ni<sub>10%</sub>/Zeolite catalyst is apparently due to the presence of reduced Ni metal (face-centered cubic crystalline structure), as was also indentified in stronger intensity in the fresh catalyst. The relatively lower intensity of the Ni metal signals might be caused by the masking effects of the carbon deposits in the spent catalyst.



**Figure 4- 5** TG and DTG profiles of the spent  $\text{Ni}_{10\%}/\text{Zeolite}$  catalysts from the KL depolymerization in ethanol-water co-solvent (50/50, v/v) at 200 and 300  $^{\circ}\text{C}$  for 1 h with FA-to-lignin mass ratio of 0.7.



**Figure 4- 6** XRD patterns for fresh Ni<sub>10%</sub>/Zeolite and spent catalyst from the 200°C test  
(▲: Zeolite X; ■: reduced Ni; ○: Carbon)

In a summary, the spent catalysts characterization results as discussed above might prove the two reasons that account for the increased BET surface area of the Ni<sub>10%</sub>/Zeolite catalyst during the kraft lignin depolymerization process in water-ethanol mixture with formic acid as an internal hydrogen source, i.e., 1) formation of amorphous fine carbon (SR,) particles of a high specific surface area on the catalyst's surface; 2) formation of amorphous structure of Al-Si oxides with a high surface area due to the collapsing of the crystalline structure of the Zeolite support.

#### 4.4. Conclusions

Catalytic reductive depolymerization of kraft lignin (KL) was investigated at 200-300 °C for 1-3 h reaction in hot-compressed water-ethanol mixture 50/50 (v/v) with formic acid as *in-situ* hydrogen source in the presence of various catalysts including Ni<sub>10%</sub>/Al<sub>2</sub>O<sub>3</sub>,

Ni<sub>10%</sub>/Zeolite, Ru<sub>10%</sub>/Al<sub>2</sub>O<sub>3</sub>, Ru<sub>10%</sub>/C and FHUDES-2. Some key conclusions drawn from this work are summarized below:

- (1) The DL yield from the KL reductive depolymerization in water-ethanol mixture (50%/50% v/v) with formic acid is determined mainly by the presence of the highly effective water-ethanol mixture with formic acid, and less on the presence of a catalyst. However, the presence of any catalyst, in particular a catalyst with acidic support, promoted the formation of SR.
- (2) FHUDES-2 (W-Mo-Ni) catalyst showed very high efficiency in sulfur-removal, and Ru<sub>10%</sub>/C exhibited excellent activity for depolymerization and hydrogenation of the depolymerized lignin products.
- (3) Ni<sub>10%</sub>/Zeolite catalyst demonstrated superb catalytic activity at a lower temperature, more active than the commercial Ru<sub>10%</sub>/C catalyst for reductive depolymerization of kraft lignin ( $M_w = \sim 10,000$  g/mol), producing 93.5 ( $\pm 4.1$ ) wt.% yield of DL of  $M_w = 3150$  g/mol at 200 °C in ethanol-water mixture (50/50, v/v) for 1 h treatment, suggesting that the expensive Ru-based catalyst can be replaced by the Ni-based catalysts for lignin reductive depolymerization.
- (4) When increasing temperature from 200 to 300 °C with or without catalyst, the yield of solid residue remarkably reduced, the  $M_w$  of DLs significantly decreased, while the DL yields remained of almost no changes. However, in the present reaction system, effect of reaction time on either the products yields or properties is minimal.
- (5) All DLs produced have a total hydroxyl number of 347-466 mg KOH/g and an aliphatic hydroxyl number of 139-326 mg KOH/g, greater than that of the original KL (275 mg KOH/g total OH number and 128 mg KOH/g aliphatic OH number). Thus, the obtained DLs can be used as a bio-replacement for petroleum-based polyols for the production of PU foam or as a phenol substitute in PF resin synthesis.
- (6) The spent catalysts characterization evidenced the formation of amorphous carbon on the catalyst's surface and formation of amorphous structure of Al-Si oxides

due to the collapsing of the crystalline structure of the Zeolite, which might account for the increased BET surface area of the spent Ni<sub>10%</sub>/Zeolite catalyst after the reaction.



## 4.5 References

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## Chapter 5 Conclusion and Recommendations for Future Work

### 5.1 Conclusions

- (1) Lignin can be an abundant natural source of aromatics (bio-phenolic chemicals or bio-polyols) after liquefaction or depolymerization.
- (2) Degraded/depolymerized lignins are more chemically reactive for the synthesis of bio-based phenolic resins, polyurethane resins and epoxy resins, as they have a smaller molecular weight, less steric hindrance effects and more active functional groups.
- (3) Many technologies, such as pyrolysis and HTL or hydrolytic depolymerization have been applied to liquefy (or de-polymerize) lignin into phenolic oils or depolymerized lignin. The oil yields are quite low in lignin pyrolysis processes, leaving a large amount of char. In contrast, HTL or hydrolytic depolymerization technology provides various benefits that are unparalleled in comparison with other technologies such as gasification, wet oxidation and pyrolysis.
- (4) The hydrolytic depolymerization mechanism involves cleaving of mainly the  $\beta$ -O-4 ether bond under base or water condition, accompanied with de-alkylation of side chains and hydrolysis of methoxyl groups.
- (5) Depolymerization of lignin can be effectively achieved by cleaving the ether bonds present in the lignin molecules with hydrogen molecules or atoms – so called reductive depolymerization. In this process, an organic solvent and a supported catalyst (such as expensive carbon-supported Pt or Ru catalysts) is needed.
- (6) The reactive hydrogen could be obtained from gaseous hydrogen in combination with suitable supported metal catalysts and a solvent medium, or from an internal or in-situ hydrogen source coming from decomposition of solvents such as formic acid and 2-propanol upon heating at elevated temperatures.

(7) The use of formic acid was found to be effective for increasing the DL yields while suppressing the formation of solid residues compared with the use of gaseous hydrogen, likely because the in situ formed hydrogen atoms (radicals) have higher mobility to lignin structure, even without the presence of a supported metal catalyst.

(8) Employing formic acid (FA) as an *in-situ* hydrogen source in ethanol/water mixture solvent media, kraft lignin (KL) was effectively depolymerized. At the optimum conditions (300°C, 1 h, ethanol-water (50/50 v/v) and FA-to-lignin mass ratio of 0.7-2.4), KL ( $M_w$  10,000 g/mol) was depolymerized into depolymerized lignin (DL) - a low-molecular weight product ( $M_w \approx 1270$  g/mol) at a high yield of  $\sim 90$  wt.%. The sulfur content was also significantly reduced from 3.1 wt% (in KL) to 0.6 wt% (in DL). The FA was demonstrated to be a more reactive hydrogen source than external hydrogen for reductive depolymerization of KL.

(9) The DL yield from the KL reductive depolymerization in water-ethanol mixture (50%/50% v/v) with formic acid is determined mainly by the presence of the highly effective water-ethanol mixture with formic acid, and less on the presence of a catalyst. However, the presence of any catalyst, in particular a catalyst with acidic support, promoted the formation of SR.

(10) FHUDES-2 (W-Mo-Ni) catalyst showed very high efficiency in sulfur-removal, and Ru<sub>10%</sub>/C exhibited excellent activity for depolymerization and hydrogenation of the depolymerized lignin products.

(11) Ni<sub>10%</sub>/Zeolite catalyst demonstrated superb catalytic activity at a lower temperature, more active than the commercial Ru<sub>10%</sub>/C catalyst for reductive depolymerization of kraft lignin ( $M_w = \sim 10,000$  g/mol), producing 93.5 ( $\pm 4.1$ ) wt.% yield of DL of  $M_w = 3150$  g/mol at 200 °C in ethanol-water mixture (50/50, v/v) for 1 h treatment, suggesting that the expensive Ru-based catalyst can be replaced by the Ni-based catalysts for lignin reductive depolymerization.

(12) When increasing temperature from 200 to 300 °C with or without catalyst, the yield of solid residue remarkably reduced, the  $M_w$  of DLs significantly decreased, while the DL

yields remained of almost no changes. However, in the present reaction system, effect of reaction time on either the products yields or properties is minimal.

(13) All DLs produced have a total hydroxyl number of 347-466 mg KOH/g and an aliphatic hydroxyl number of 139-326 mg KOH/g, greater than that of the original KL (275 mg KOH/g total OH number and 128 mg KOH/g aliphatic OH number). Thus, the obtained DLs can be used as a bio-replacement for petroleum-based polyols for the production of PU foam or as a phenol substitute in PF resin synthesis.

(14) The spent catalysts characterization evidenced the formation of amorphous carbon on the catalyst's surface and formation of amorphous structure of Al-Si oxides due to the collapsing of the crystalline structure of the Zeolite, which might account for the increased BET surface area of the spent Ni<sub>10%</sub>/Zeolite catalyst after the reaction.

## 5.2 Recommendations for Future Work

To continue the research conducted for this thesis, it is recommended to use continuous flow reactor to make it into continuous process. Because the economic profile for batch reactor is limited and labor-intensive. Furthermore, several reaction models and reactor models are needed to demonstrate the feasibility of this research. The response surface method can be used to explore the relationships between several variables and determine the optimal operating conditions.

Although the Ni<sub>10%</sub>/Zeolite was shown to have great effect at low temperature, model compound studies are needed to study the mechanism. In addition, activity of the spent catalysts after regeneration shall be tested for a few cycles to evaluate the life-time of the catalyst. To further enhance the activity and lifetime of the Ni<sub>10%</sub>/Zeolite catalyst, promoters (such as Mo, Co, P, B, etc.) should be investigated.

Moreover, black liquor, instead of pure lignin, can be utilized as a crude and inexpensive lignin source for the depolymerization study for fuels and chemicals production.

## Appendices



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**Author:** Dinesh Mohan,<sup>\*,†,‡</sup> Charles U. Pittman, Jr.,<sup>†</sup> and Philip H. Steele<sup>§</sup>

**Publication:** Energy & Fuels

**Publisher:** American Chemical Society

**Date:** May 1, 2006

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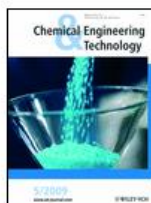
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**Author:** M. P. Pandey, C. S. Kim  
**Publication:** Chemical Engineering & Technology  
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**Title:** Hydrothermal degradation of alkali lignin to bio-phenolic compounds in sub/supercritical ethanol and water-ethanol co-solvent

**Author:** Shuna Cheng,Carolynne Wilks,Zhongshun Yuan,Mathew Leitch,Chunbao (Charles) Xu

**Publication:** Polymer Degradation and Stability

**Publisher:** Elsevier

**Date:** June 2012

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**Title:** Catalytic depolymerisation and conversion of Kraft lignin into liquid products using near-critical water

**Author:** Thi Dieu Huyen Nguyen, Marco Maschietti, Tallal Belkheiri, Lars-Erik Åmand, Hans Theliander, Lennart Vamling, Lars Olausson, Sven-Ingvar Andersson

**Publication:** The Journal of Supercritical Fluids

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<b>Honours and Awards:</b>	Western Graduate Research Scholarship Faculty of Engineering, Western University 2011-2013
<b>Related Work Experience</b>	Internship Gaoqi Energy Engineering Co., Ltd, Guangzhou, GD 07/2011-08/2011

### Publications:

#### Peer-reviewed Journals

1. Structure, Antibacterial Activities and DNA Interaction of a Copper( II ) Complex with 2-(2'-Pyridyl) benzoxazole and Glycinate. Chinese Journal of Inorganic Chemistry, 2012, 28(8), 1580-1586.
2. Study on Chitosan Diguanidinylated Coating Preservation of Longan and Its antifungal activities. Science and Technology of Food Industry, 2012, 33(18), 328-331.
3. Reductive degradation of Kraft lignin into bio-chemicals & fuels using formic acid as an in-situ hydrogen source – accepted. Bioresource Technology.
4. Catalytic reductive de-polymerization of Kraft lignin for chemicals and fuels – in progress. Bioresource Technology.

### Conferences Presentations

1. Huang, S., Yuan Z, Tymchyshyn, M., Xu C\*. “Lignin depolymerization for bio-chemicals and bio-fuels with formic acid”, *The LignoworkAGM presentation*, Cornwall, ON, Canada, May, **2013** (Oral presentation)
2. Huang, S., Yuan Z, Tymchyshyn, M., Xu C\*. “Catalytic depolymerization of kraft lignin in the presence of formic acid”, *The LignoworkAGM presentation*, Vancouver, BC, Canada, June, **2014** (Oral presentation)